Volume 31, Number 12

December, 1961

JOURNAL OF GENERAL CHEMISTRY of the USSR

ЖУРНАЛ ОБЩЕЙ ХИМИИ
(ZHURNAL OBSHCHEI KHIMII)

TRANSLATED FROM RUSSIAN

CONSULTANTS BUREAU

Volume 31, No. 12
December, 1961

JOURNAL OF
GENERAL CHEMISTRY
OF THE USSR

(ZHURNAL OBSHCHEI KHIMII)

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:
Vol. 19 No. 1 January 1949

	U. S. and Canada	*Foreign*
Annual Subscription	*$160.00*	*$165.00*
Annual subscription for libraries of nonprofit academic institutions	*50.00*	*80.00*
Single issue	*20.00*	*20.00*

Copyright © 1962
CONSULTANTS BUREAU ENTERPRISES, INC.
227 West 17th Street, New York, N. Y.

Editorial Board
(ZHURNAL OBSHCHEI KHIMII)

A. E. Arbuzov, S. N. Danilov (Editor-in-Chief), N. A. Domnin
(Assistant Editor), E. D. Kaverzneva, M. A. Klochko,
K. P. Mishchenko, A. A. Petrov, B. V. Ptitsyn
S. A. Shchukarev, E. D. Venus-Danilova
Yu. K. Yur'ev, A. I. Zakharova
(Secretary)

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners.

Printed in the United States of America

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 31, Number 12 December, 1961

CONTENTS

	PAGE	RUSS. PAGE
Some Important Tasks for Chemistry in the Light of Resolutions of the 22nd Congress of the CPSU	3585	I
Recollections of Academician V. E. Tishchenko. N. I. Nikitin	3589	3849
Study of the Alkaline Decomposition of Isopropylbenzene Hydroperoxide. I. Some Properties of the Hydrated Sodium Salt of Isopropylbenzene Hydroperoxide. V. A. Belyaev and M. S. Nemtsov	3594	3855
Study of the Alkaline Decomposition of Isopropylbenzene Hydroperoxide. II. Some Properties of the Anhydrous Sodium Salt of Isopropylbenzene Hydroperoxide. V. A. Belyaev and M. S. Nemtsov	3599	3861
Polarography of Diphenylcyclopropenone. S. I. Zhdanov and M. I. Polievktov.	3607	3870
Polarography of Diethylaminoethylmercaptan. S. I. Zhdanov	3611	3874
Investigation of the Hydrolysis of Salts of Methyl Sulfuric and Ethyl Sulfuric Acids by the Isotope Method. I. P. Grazerov and A. M. Tarasenko	3615	3878
Reactions of Aliphatic Diazo Compounds with Unsaturated Compounds. XX. Investigation of the Reaction of Ethyl Diazoacetate with 1-Phenylpropyne in the Presence of Copper Sulfate. I. A. D'yakonov and M. I. Komendantov	3618	3881
Catalytic Synthesis of β-Arylamino Ketones. N. S. Kozlov and A. D. Nikolaev.	3629	3894
Synthesis of Acetals of Vinylacetylenic Aldehydes. V. B. Mochalin and N. G. Ivanova	3632	3896
Synthesis of O-Aminoacyl Derivatives of Adenosine and a Study of Their Properties. É. Ya. Dreiman, V. A. Dmitrieva, S. G. Kamzolova, Z. A. Shabarova, and M. A. Prokof'ev	3635	3899
Research in the Field of Glycol Ethers and Their Derivatives. XXXIX. Synthesis of Aromatic γ-Chloroethers. Shamkhal Mamedov and D. N. Khydyrov	3641	3905
2,5-Dimethoxy-2,5-dihydrofurfuryl Benzoates and Some of Their Reactions. N. K. Kochetkov, L. I. Kudryashov, N. V. Molodtsov, and E. D. Khomutova	3645	3909
The Mechanism of the Reaction of Cyanamide with Monobasic Fatty Acids. A. E. Kretov and A. P. Momsenko	3651	3916
Furanidinopyrazoles. I. K. Korobitsyna, Yu. K. Yur'ev, Yin Ch'ên-lieh, A. F. Davydova, and N. N. Gaidamovich	3656	3921
Steric Hindrance in 4,4'-Diarylthiazolocyanine Molecules. E. D. Sych and A. I. Kiprianov	3661	3926
S-Derivatives of Thiourea. IV. Preparation of 2-Bromo-3-isothiuroniumpropylamine and Study of Some of Its Transformations. V. M. Fedoseev, V. N. Bochkarev, and A. B. Silaev	3664	3929
Syntheses of Secondary Amines of the Thiophene Series. B. P. Fedorov, G. I. Gorushkina, and Ya. L. Gol'dfarb	3668	3933

(continued)

CONTENTS (continued)

	PAGE	RUSS. PAGE
Stereochemistry of Cyclic Compounds. XLIII. Stereochemistry of the Diene Condensation of Trans-1-vinyl-6-acetoxy-9-methyl-Δ^1-octahydronaphthalene with Maleic Anhydride and Some Transformations of Dicarboxylic Acids of the Dodecahydrophenanthrene Series. I. A. Gurvich, I. M. Mil'shtein, and V. F. Kucherov	3674	3939
The Preparation of Allene. Ya. M. Slobodin and A. P. Khitrov	3680	3945
Organic Insectofungicides. LXI. Synthesis of Some Mixed Ethylmercaptoethyl Thiophosphates. Ya. A. Mandel'baum, N. N. Mel'nikov, Z. M. Bakanova, and P. G. Zaks	3682	3947
Organic Insectofungicides. LXII. Synthesis of Some New Derivatives of Phosphonoacetic Acid. N. N. Mel'nikov, Ya. A. Mandel'baum, V. I. Lomakina, and V. S. Livshits	3684	3949
Organic Insectofungicides. LXIII. Synthesis of Some Phosphinic Acid Derivatives. N. N. Mel'nikov, Ya. A. Mandel'baum, and Z. M. Bakanova	3687	3953
Cyanine Dyes Containing Fluorine. X. Cyanine Dyes Containing Fluorine in the Polymethyne Chain. L. M. Yagupol'skii and B. E. Gruz	3690	3955
2-Trifluoromethylnaphthalene and Its Derivatives. II. L. M. Yagupol'skii, Yu. A. Fialkov, and P. A. Yufa	3696	3962
Investigations of Benzimidazole Derivatives. VIII. Amination of Some 1-Substituted Benzimidazoles. A. M. Simonov and A. F. Pozharskii	3703	3970
β-Dicarbonyl Compounds. XIV. Synthesis, Conversions, and Biological Activity of Derivatives of 2-(3'-Methyl-2'-butenyl)-dihydroresorcinol. V. I. Gunar, S. I. Zav'yalov, G. N. Pershin, S. N. Milovanova, N. S. Bogdanova, O. O. Makeeva, and A. I. Krotov	3707	3975
Anthraquinone Derivatives. I. Synthesis of Chloro Derivatives of 2-Anthraquinonecarboxylic Acid. N. S. Dokunikhin, Z. Z. Moiseeva, and S. N. Burenko	3716	3985
β-Dicarbonyl Compounds. XV. Chemical Properties of 1,3-Dichlorocyclohexadiene-1,3 and Its Derivatives. S. I. Zav'yalov and G. V. Kondrat'eva	3719	3987
Aryltrifluoromonohydrides of Phosphorus. Zh. M. Ivanova and A. V. Kirsanov	3723	3991
Imidazole Derivatives. XXVI. A. V. El'tsov and L. S. Éfros	3726	3994
Chemical Activity and Steric Accessibility. I. Reaction of Arylmagnesium Halides with Chloro Ethers. I. I. Lapkin and R. G. Mukhina	3732	4001
New Methods of Preparing Esters and Ester-Acid Chlorides of Selenious Acid. N. N. Yarovenko, M. A. Raksha, and G. B. Gazieva	3737	4006
Reaction of Difluoromethyl Difluoroacetate with Potassium Fluoride. N. N. Yarovenko and M. A. Raksha	3742	4011
Synthesis of Some Amino-1,3,4-oxadiazoles. A. P. Grekov and V. I. Grigor'eva	3743	4012
Action of Carbon Disulfide on Sodium Diethylphosphite. B. A. Arbuzov, É. N. Dianova, and R. R. Shagidullin	3746	4015
Organoboron Compounds. LXXXVII. Action of Diborane on Aryl Derivatives of Boron. B. M. Mikhailov and V. A. Dorokhov	3751	4020
Steric Hindrance and Reactivity of Organic Compounds. III. Isomerization of 1,8-Dihalonaphthalenes in the Presence of Anhydrous β-Naphthalenesulfonic Acid. V. A. Koptyug, V. G. Shubin, and V. A. Plakhov	3754	4023
Polyethylene Glycols and Some of Their Derivatives. A. N. Pudovik and T. M. Moshkina	3759	4028
Addition of Aromatic Derivatives to Vinylmethyldichlorosilane. K. A. Andrianov, A. A. Zhdanov, and V. A. Odinets	3764	4033
Hydrolysis of Cyclic Polymethylsilazanes. K. A. Andrianov and G. Ya. Rumba	3768	4038
Preparation of Hemi-Chloronitroso Hydrocarbons. A. E. Kretov, E. A. Abrazhanova, and S. I. Zlotchenko	3772	4043

CONTENTS (continued)

	PAGE	RUSS. PAGE
Synthesis and Investigation of Aminodesoxy Sugars. II. N-Aryl Derivatives of 6-Amino-6-desoxydiacetone-D-galactose. V. I. Veksler	3774	4045
Synthesis of Diacid Chlorides of Alkylselenophosphinic Acids. S. Z. Ivin and I. D. Shelakova	3780	4052
New Method of Synthesizing Phosphinic and Thiophosphinic Esters. XXXVI. Synthesis of Phosphinic Acid Derivatives with Cyclic Radicals in the Ester Groups. A. N. Pudovik and G. P. Krupnov	3782	4053
LETTERS TO THE EDITOR		
Some Reactions of Heteroorganic Compounds of Group IV Catalyzed by Aluminum Chloride. G. A. Razuvaev, N. S. Vyazankin, O. S. D'yachkovskaya, I. G. Kiseleva, and Yu. I. Dergunov	3784	4056
Photoreaction of Carbon Tetrachloride with Dioxane. G. A. Razuvaev, N. S. Vasileiskaya, V. T. Bychkov, and A. E. Makar'eva	3785	4057
Conversion of Tricyclohexenones to Tricyclohexenylamines. M. N. Tilichenko, N. S. Barbulescu, and V. I. Vusotskii	3787	4058
Some Rules in the Mass Spectra of Monoolefins. A. A. Polyakova and R. A. Khmel'nitskii	3789	4059
Acrylyl- and Methacrylylpyrrolidones. F. P. Sidel'kovskaya, M. G. Zelenskaya, and M. F. Shostakovskii	3791	4060
DISCUSSION		
Nature of Si—O Bonds and Interatomic Distances in Silicates. A. N. Lazarev	3792	4061
Preparation of Monosaccharide Derivatives in the Furanose Form. A. A. Abramzon and M. V. Ostrovskii	3794	4062
Author Index, Volume 31, 1961	3799	
Tables of Contents, Volume 31, 1961	3821	

SOME IMPORTANT TASKS FOR CHEMISTRY IN THE LIGHT OF RESOLUTIONS OF THE 22ND CONGRESS OF THE CPSU

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. I-IV, December, 1961

At its 22nd congress, the Communist Party of the Soviet Union gave the results of the universal-historical victories of the Soviet people in the fight for the triumph of communism during the time which has elapsed after the 20th congress, and adopted a new Program. The 22nd congress satisfactorily demonstrated the great unity of our Leninist Party and the monolithic solidarity of the whole Soviet people around it. In addition, the congress was a clear demonstration of the solidarity and monolithic nature of the international communist movement. The congress fully approved the resolute measures taken by the Leninist Central Committee, headed by comrade N.S. Khrushchev, on overcoming the consequences of the Stalin personality cult, on the exposure and ideological destruction of the anti-Party group of Molotov, Kaganovich, Malenkov, and others, who have come out against the course designated by the 20th congress and have attempted to divert the Party and the country from the Leninist path. The resolutions of the 22nd congress have produced an extremely great rise in the polytechnical and laboring work and the creative activity of workers, collective farmers, and the intelligentsia of the Soviet Union.

All Soviet people have approved eagerly and with their whole souls the resolutions of the congress and the new Program of the CPSU, which are imbued with the Party slogan: "All in the name of man and for the good of man." The 22nd congress of the CPSU has exerted an enormous revolutionary influence on the development of the route of progress of the whole of humanity. A resolution of the congress confirmed that: "at the present time it is not imperialism but socialism that determines the main direction of world development." The new Program of the CPSU, adopted by the 22nd congress, is a clear and definite Marxist-Leninist plan for the development of the whole life of our Soviet society and our whole Soviet people. The congress allotted great importance to the question of the further development of Soviet science and culture and confirmed with great force the importance of science for the progress of all branches of the national economy and for the further development of culture and ideology.

The Program of the CPSU requires that "with us, science – as Lenin said in 1923 – should not remain a dead letter or a fashionable phrase ..., that science should actually enter our flesh and blood and be fully and genuinely transformed into a component element of our life."*

Developing Lenin's policy for science further, the congress confirmed that communism and science are inseparable.

The scope of scientific investigations and their connection with practical activity must attain that level at which, as is noted in the Program, "science becomes in full degree a direct productive force." During the years of Soviet rule, in a number of divisions of physics, mathematics, chemistry, biology, and geology, our science has actually occupied leading positions.

The resolution of the Central Committee of the CPSU and the Council of Ministers of the USSR "on measures for the improvement of coordination of scientific investigations in the country and the activity of the Academy of Sciences of the USSR" has enormous importance for the organization and planning of the development of science in the USSR. The conference of scientific workers which took place in the Kremlin in the summer of this year considered means for the further development of science and questions of its approach to the practice of communistic construction in the light of this resolution. In our time, the progress of industry and the progress of science are indissolubly linked with one another. It is pointed out in the party's Program that "a guarantee of the fruitful development of science lies in the indissoluble link with the creative labor of the people and the practice of communist construction The tasks laid down in the Program demand a further increase in the level and purposefulness of scientific investigations and of their indissoluble link with practice. Simultaneously with these resolutions, the congress emphasized that the

* V.I. Lenin. Works. Vol. 33, p. 447.

development of broad theoretical trends in science must be accelerated and must have the efforts of our scientists concentrated upon them. All these questions will be dealt with by the State Committee on the coordination of scientific research work together with the Academy of Science and other scientific institutions.

The Program of the CPSU noted that complex and many-sided problems must be solved by chemical science. First of all, a further increase in the level and purposefulness of scientific chemical investigations, the determination of the most current and pressing problems which have the greatest importance and specific gravity both for the development of theoretical chemistry and for the performance and solution of the most vital and effective industrial tasks must be achieved. An even closer linkage of scientific investigations with practical life and with the chemical and other branches of industry and the national economy must be established. One of the main tasks in the development of chemistry must be the creation of cheap synthetic materials for all branches of the national economy and for the daily and cultural life of the Soviet people.

The resolution of the May Plenary Session of the Central Committee of the CPSU in 1958 provoked a considerable increase in scientific investigations on the chemistry of high molecular weight compounds, and polymers in particular. In fulfilling this resolution, scientists and industrial workers developed new effective processes and methods for producing various polymers and initial monomeric substances. Thus, questions of the industrial production of new synthetic materials, for example, polypropylene, have been developed, and are being developed further. Additional new methods for the industrial production of a whole series of synthetic fibers and many valuable materials from the simplest natural gas and petroleum raw materials have been found and are being developed.

The wide practical use of polymers impels chemists to search for such methods of synthesis as may lead to the production of materials possessing properties suitable for application in various fields of the national economy. In this connection, fundamentally new approaches to the process of polymerization and new ways and methods for the production of polymeric materials have been found. For example, "graft polymerization," "block polymerization," and the synthesis of spatially strictly "stereoregular" polymers are being developed.

In a number of sections of the chemistry of polymers, we are going ahead of foreign countries; this is particularly characteristic and fundamental in the field of heteroorganic high molecular weight compounds. For example, the successful synthesis of heat-stable dielectrics used in electrical technology, radioelectronics, and other branches of the new technology must be mentioned. These polymers make it possible to work with high specific energy and heat loads at high electrical densities. The chemists have the task of developing and obtaining such synthetic fibers as will be stronger than steel in order that automobile tires may last much longer and that parts of plastic are introduced more widely into machine construction.

The high level of the development of technology with its unprecedentedly high rates, pressures, and temperatures demands the creation of new synthetic materials not found in nature. In this connection, the discovery and development of new methods for the production of inorganic polymers, as being the most stable and possessing the necessary properties, have the greatest prospects.

There are inexhaustible sources of raw materials for the production of these polymers and the development of chemistry in this direction will have enormous theoretical and practical consequences. Possessing great strength, stability, and resistance to oxidation, these polymers will replace metals to a considerable degree. Organosilicon polymers, even at present, have found very diverse and wide applications in industry and technology both as hard and heat-resistant materials and as liquid oils, greases, and hydrophobic coatings.

The problem of producing high molecular weight compounds, polymers and plastics, synthetic fabrics, leathers, rubbers, and other materials, as is well known, is closely connected with another no less important and pressing problem – the chemistry of monomers. Here there is the concrete task of finding and synthesizing monomeric compounds capable or potentially capable of undergoing polymerization under various conditions. There is no doubt that this enormous and pressing problem must be divided between very diverse laboratories of scientific research institutes and university departments. Here work by all will suffice and be taken up rapidly by special high molecular weight institutes and laboratories. It may confidently be expected that many results of the work of individual investigators and research groups will not be favored in full measure with the attention of the appropriate scientific and applied institutes. In overcoming this irregular practice, there are great reserves for the development of the chemistry of valuable and diverse polymers. We must use these reserves to the maximum possible extent. For the same purpose, we should, in many cases, accelerate the organization and equipment of special laboratories for the chemistry of monomers. All the above measures could considerably widen and consolidate the in-

dustrial production of polymers and solve the problem to which our Party has attached such great importance with greater rapidity.

In the Program and resolution of the 22nd Congress of the CPSU, great importance was given to the problem of the "chemicalization" of agriculture, biology, and medicine. But among the great complex of questions here, a particularly important role is played by the production and use of new substances necessary for the regulation and improvement of living processes in the human, animal, and plant organisms. Thus, to increase the yield and productivity of animal husbandry, the use of trace quantities of a number of chemical elements and compounds gives a great effect. A considerably greater scope must be given to the search for new methods of a synthesis of various biologically active substances such as vitamins and, in particular, substances having great importance in medicine and animal husbandry. The question of the development of syntheses of highly effective preparations to be used in the fight against agricultural pests is also pressing. The chemical industry must rapidly organize the production of these substances.

In the resolutions of the 22nd Congress of the CPSU, particular attention was devoted to the setting up of teams of higher qualification – doctors of science – and also to the creation of the necessary conditions for raising the qualification and scientific development of young co-workers of scientific establishments. The problem of setting up and training qualified scientific teams is considered as the most important and paramount – as problem No. 1.

The heartfelt gratitude to Soviet scientists expressed by N.S. Khrushchev inspires us all, workers in science, to new creative daring and to selfless labor in the name of the creation of communism.

VYACHESLAV EVGEN'EVICH TISHCHENKO
(1861-1941)

RECOLLECTIONS OF ACADEMICIAN V.E. TISHCHENKO

N.I. Nikitin

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3849-3854, December, 1961
Original article submitted July 5, 1961

The present year marks the centenary of the birth of Academician Vyacheslav Evgen'evich Tishchenko. V.E. Tishchenko was born in St. Petersburg August 7, 1861. When his father died, V.E. was only 16 years old, and he found himself the oldest among the remaining six children. V.E., then studying at the high school, began to give lessons in order to earn money. On finishing high school, in 1879 he entered the natural division of the physico-mathematical faculty of the University of St. Petersburg, which he completed in 1884.

The scientific activity of V.E. Tishchenko began in 1883, when he was still a student on the above course, in the laboratory of A.M. Butlerov.

On completing his university studies, V.E. was retained for training for professorial status [1]. A.M. Butlerov proposed that he should study the action of the hydrogen halide acids on formaldehyde. The products of this reaction proved to be the halogenomethane and formic acid [2]. Subsequently, V.E. made a detailed investigation of the action of dry hydrogen halides on formaldehyde and obtained the first symmetrical dihalogenomethyl esters [3]. Starting with these investigations, he then went deeper into this field: he studied the action of halides on formaldehyde and showed that this led to the formation of halogenooxides [4]. By the action of zinc ethyl on trioxymethylene V.E. obtained n-propyl alcohol, and by the action of zinc propyl he obtained n-butyl alcohol [5]. V.E. had to prepare the trioxymethylene himself by the oxidation of methanol vapors with air over a platinum catalyst. V.E. prepared some hundreds of grams of trioxymethylene; A.M. Butlerov was very proud of such large (for those times) amounts and showed this preparation to visitors.

In 1884, V.E. Tishchenko transferred to D.I. Mendeleev with the position of personal assistant. Mendeleev was then very interested in questions of the petroleum industry and the formation of petroleum. A large and complex investigation was then carried out by V.E. by fractionating and studying the properties of the fractions of Baku, and then of American, petroleum. On careful fractionation of petroleum, remarkable points on the curve of the change of specific gravity of the fractions were observed which corresponded to the presence of individual hydrocarbons in the fractions. A comparison of the distillation curves of Caucasian and American petroleum was carried out, and the composition and density of the vapor were determined. This work occupied V.E. four years. Under D.I. Mendeleev's directions, V.E. also worked on the study of the hydrates of sulfuric acid ($SO_3 \cdot 2H_2O$) and alcohol ($C_2H_5OH \cdot 3H_2O$). The existence of such hydrates followed from the well-known work of D.I. Mendeleev on the determination of the change of density of solutions of sulfuric acid and alcohol. These investigations were carried out by V.E. with unusual care. In subsequent years, recalling his association with D.I. Mendeleev, V.E. published several papers devoted to memories of his great teacher [6].

The strict methods of analysis of chemical compounds which he mastered in his youth in the laboratories of A.M. Butlerov and D.I. Mendeleev were used by V.E. constantly in the course of his whole life.

We shall pass now to the later experimental work of V.E. Tishchenko. On one occasion, one of the owners of a large brewery turned to D.I. Mendeleev with a request to improve the quality of the beer produced. Mendeleev appointed V.E. Tishchenko. V.E. carefully studied every stage of the industrial process, organized a laboratory at the brewery, and soon, in fact, worked out a method for producing very good beer which stood up to the competition of better breweries. This work was not published but its results entered in part into V.E.'s investigation on the various types of our native brewing barleys [7].

In 1893, the Council of the University of St. Petersburg sent the 32-year-old assistant professor V.E. Tishchenko to the USA to the World Columbus Exhibition. V.E. was included in a number of Russian experts in the International Expert Commission. The result of this service was an extremely thorough investigation of the tree-tapping industry

in the USA, a detailed account of which V.E. gave in a well-known fundamental monograph [8]. It is impossible to dwell in detail on this interesting book in our short sketch.

In 1896, V.E. Tishchenko began another important applied chemical investigation on improving the quality of Russian chemical glass. Our chemical glass could not compete with Jena glass and it was felt necessary to improve the formulation used in its preparation in order to obtain completely satisfactory chemical glassware. After 3 years' careful experimental work, V.E. magnificently coped with this problem. Glass for chemical vessels prepared according to V.E. Tishchenko's formulation has been widely used in all our country's laboratories since that time. The testing of this chemical glass, repeated in 1927, showed that no change in the composition of the charges for it were required in respect to its main types. Some articles of Russian chemical glass were shown at the Paris Exhibition of 1900 [1] and it received a first class prize. Later, while living not far from Luga, V.E. turned his attention to the local white sands and investigated their properties in detail, and as a result of this work these sands came into use in the factories of the Leningrad region and some others [9]. V.E., taking part in the creation of the production of optical glass in our country and promoting it with his knowledge, worked in association with I.V. Grebenshchikov, N.N. Kachalov, and others.

In 1899 V. E. defended a magisterial thesis on the subject of "The Action of Amalgamated Aluminum on Alcohol" [10]. This work is a classic and together with his subsequent investigations on "The Action of Aluminum Alkoxides on Aldehydes" won for V.E. an honorable position among the leading chemists of that time. V.E. showed that carefully amalgamated aluminum reacts with an anhydrous alcohol liberating hydrogen and giving an aluminum alkoxide. Broadening this investigation, V.E. proposed a method for the production of absolutely pure aluminum alkoxides of the whole alcohol series and studied the properties of the alkoxides, formerly known only in general outlines, in very great detail. In studying the thermal decomposition of the aluminum alkoxides and, incidentally, the pyrolysis of alcohols, aldehydes, and ethers, V.E., together with student A. Grigor'ev, made the very important discovery that alumina has the property of catalyzing the decomposition of alcohols into ethylenic hydrocarbons and water [11] at 400-450° extremely energetically and smoothly. This discovery then became incorrectly ascribed to V.N. Ipat'ev, who continued the development of the reaction first carried out by V.E. Tishchenko and A. Grigor'ev.

Somewhat later, studying the action of aluminum alkoxides on acetaldehyde, V.E. discovered an absolutely new way of condensing the aldehyde and converting it into ethyl acetate. This oberservation was transferred to other aldehydes [12]. Using the aluminum alkoxides obtained as condensing agents, V.E. achieved smooth conversions of various aldehydes into the corresponding esters in all cases. This work of V.E.'s was used for the practical preparation of a series of esters forming valuable sovents, etc.

In 1900, V.E. Tishchenko again took up investigations on the chemistry of wood and published a communication on the composition of the soft resin of Pinus silvestris and a comparative investigation of fir and Canada balsams [13]. This work was carried out in association with the student Petrov and it showed for the first time that the ordinary Russian pine can give a soft resin with the same good yield of turpentine (18-19%) as the soft resin from the American long-coned pine and the French resin from the maritime pine In another part of this work, the results of an investigation of fir balsam from the Siberian fir in comparison with Canada balsam from Abies canadensis were given. Important conclusions were drawn on the possibility of replacing imported Canada balsam with domestic fir balsam.

In 1918, V.E. was elected director of the laboratory of chemical reagents in the State Institute of Applied Chemistry.

For about 15 years he directed the research work and took part in the creation of methods of producing chemically pure preparations of lead acetate, copper oxide, manganese peroxide, and a number of other substances not previously manufactured in the USSR. V.E. frequently pointed out new methods for the production of such preparations, often using the waste products of other industries. Here he turned his attention to a method which he proposed in 1930 with S.A. Smirnov of obtaining liquid gold and silver for painting china [1]. Much later, V.E. Tishchenko and A.P. Sidorkin published their work on the production of zirconium dioxide from Khibiny apatite [14].

In 1927, for numerous and extremely beneficial scientific investigations, V.E. was elected a Corresponding Member of the Academy of Sciences of the USSR.

In subsequent years, the scientific interest of V.E. Tishchenko became concentrated more and more on questions of wood chemistry and on the use of wood chemicals – resins turpentine, acetone oil, and ketones conveniently obtained by the dry distillation of wood, etc.

In 1931, V.E. Tishchenko in collaboration with A.G. Evdokimov published a paper on the purification of the waste material from the sulfate cellulose industry, the so-called "sulfate" turpentine [15]. The difficulty in purifying this turpentine from sulfur-containing impurities consisted in the fact that, after it, the turpentine again acquired a strong smell on storage. As is known, there are a number of methods for the purification of "sulfate" turpentines described in patents which, however, have not been tested under Russian conditions. Tishchenko and Evdokimov's method was worked out on the plant product; it consists essentially of treating the turpentine with iron turnings and dilute hydrochloric acid to reduce the disulfide $CH_3-S-S-CH_3$ to mercaptan. The mercaptan was then distilled off in large part with steam. The authors investigated the composition of the purified sulfate turpentine by Darmois's method and showed that it consisted of 75% of dextro-α-pinene, 19% of destro-Δ^3-carene, and 2% of high-boiling fractions.

In 1930, V.E., together with M.I. Leshkevich and L.A. Skul'ska, published a paper on birch still resin obtained as a by-product in the distillation of the acid aqueous distillate from the dry distillation of wood [16]. This resin had been extremely little studied in view of the difficulties which arise in separating mixtures of such complex composition. A large part of the resin was burned under the boilers or used for the preparation of brickettes from sawdust and the like. V.E. and his co-workers, using vacuum distillation isolated and identified, in addition to formic and acetic acids, angelic acid, a ketoalcohol – methylcyclopentenolone – 4-hydroxy-3,5-dimethoxy-1-methylbenzene, and other products. At the same time, the authors showed the possibility of making practical use of birch still resin by using the high reductive capacity of its oil for development in photography and for pharmaceutical purposes.

In 1931, together with L.I. Antsus [17], V.E. published a paper on the composition of the white acetone oil obtained in the form of a by-product in the dry distillation of calcium acetate in the production of acetone. This work was also carried out in the style of classical organic investigations and, as a result, the authors isolated from white acetone oil and identified: acetaldehyde and propionaldehyde, acetone (8%), sylvane (0.5%), methyl ethyl ketone (22%), methyl isopropyl ketone, methyl propyl ketone (19%), methyl isobutyl ketone, methyl butyl ketone, and mesityl oxide. The practical significance of this investigation was the possibility of the technical production in this way of a number of the ketones mentioned in the production of acetone from calcium acetate.

In 1934, V.E. Tishchenko and N.V. Koshkin [18] developed a method for determining the pentosans in vegetable materials in which the amount of furfural liberated on acid hydrolysis is determined by precipitation with dephenylthiobarbituric acid.

The main direction of V.E.'s work in the field of wood chemistry in the 'thirties was the development of a completely new method for the catalytic production of camphor from turpentine. These investigations were carried out in the Leningrad Scientific Research Institute of Wood Chemistry, where V.E.'s assistants in carrying out the laboratory investigations and experiments on the pilot plant were G.A. Rudakov, M.A. Grekhnev, S.Ya. Korotov, D.K. Andreev, and other chemists.

In developing the new catalytic process for the production of camphor from turpentine consisting mainly of α-pinene, V.E. made use of an observation of L.S. Gurbich's on the action of bleaching clay (floridin) on pinene, as a result of which camphene and other isomers, and polyterpenes, were obtained. In 1928, V.E. and V.Y. Marga [19] confirmed the scheme for the isomerization of α-pinene and showed that kaolin, floridin, and bauxite were distinguished in their isomerizing action on pinene only in the strength of their polymerizing capacity (formation of by-product polyterpenes). It was then found [20] that the isomerization of α-pinene into camphene goes well under the action of various finely-dispersed clays, best when activated with hydrochloric acid. Treatment of the camphene obtained with formic (or acetic) acid then led to the formic ester of isoborneol, saponification of which yielded borneol. The catalytic dehydrogenation of the latter led to camphor. This "isomerization" process for the production of camphor developed by V.E. and his co-workers proved much simpler than the pinene hydrochloride method. All stages of the process were carefully worked out and experimental apparatus was constructed, after which, in 1938, the first factory for artificial camphor was put into operation [21].

The work of V.E. and his students on the isomerization of terpenes under the action of activated clays led to the creation of our domestic industry for the production of synthetic camphor. These investigations were honored with a Stalin prize. They attracted the attention of chemists in foreign countries to the possibilities of using aluminosilicates as catalysts for all kinds of isomerization processes.

In the last years of his life, V.E., with his students, carried out a number of studies on the employment of the investigation of L.A. Chugaev on the heat-decomposition of xanthates for the case of glycols and the corresponding dibromides [22]. As a result, a method was proposed for the production of the corresponding dienes and acetylenes.

These studies excited great interest in the heat-decomposition of esters which did not die out until recent times and opened up great possibilities for science and technology (synthesis of dienes, unsaturated acids, etc.).

V.E. Tishchenko was scientific secretary of the Chemical Division of the Russian Physico-chemical Society for 40 years and Professor of Technical and Analytical Chemistry of the University of St. Petersburg (Leningrad) for about 45 years. His work in the Chemical Society formed a remarkable example of public service. V.E. was the real organizer of the meetings of the Chemical Division, directed its work, managed the compilation of notices of meetings and the printing of their minutes, conducted all the communication with foreign scientists, was actively interested (with T.V. Volkova) in the exchange of journals and in the library generally, and was the organizer of a commission on the award of prizes. In the period from 1900 to 1915, V.E. delivered a course of general and organic chemistry at the Women's Medical Institute. From 1912 to 1915 he occupied the position of prospector of the University of St. Petersburg, and from 1915 to 1918 that of the Dean of the Faculty of Physics and Mathematics. In 1937, V.E. was elected a Corresponding Member of the Academy of Sciences of the USSR.

In 1938, V.E. published, together with M.N. Mladentsev (also a former student of D.I. Mendeleev) volume 1 of a biography of Dmitrii Ivanovich. The collection of material for the biography occupied several years' work, but the authors wrote in the preface that they considered this work their moral duty to the memory of their great teacher.

In 1937, the presidium of the Academy of Sciences of the USSR named V.E. president of the then newly formed commission on cellulose. Under his direction, two all-union conferences on cellulose were called. It is interesting to note that even at that time the question of the creation of a special scientific institute on the chemistry of high molecular weight compounds within the framework of the Academy of Sciences of the USSR was raised in one of these communications.

V.E.'s creative energy was not affected by a life of considerable tensions. Among them, one imperialistic war robbed V.E.'s family of two sons. Once, during a walk in a wood in the neighborhood of Luga, he spoke of this loss as if he was going to the frontal area to find his eldest son's grave.

V.E. Tishchenko was extremely well disposed to people and always ready to listen to those who turned to him for advice or information. He never raised his voice, but enjoyed such great and universal esteem that his mere presence was sufficient to enrich any conversation and to elevate any discussion of a scientific question to its proper height. V.E. died in 1941.

The clear recollection of V.E. Tishchenko will always revive in our thoughts that outstanding period in the development of our national chemistry in which he played a part together with those leading representatives of our national science, D.I. Mendeleev and A.M. Butlerov.

LITERATURE CITED

1. N.A. Orlov. "Outline of 50 Years' Scientific Activity of Prof. V.E. Tishchenko; A Collection of Selected Works of V.E. Tishchenko" [in Russian] (ONTI, 1934), p. V.
2. V.E. Tishchenko, ZhRPhKhO 15, 381 (1883); 16, 461 (1884).
3. V.E. Tishchenko, ZhRPhKhO 18, 433 (1886); 19, 464 (1887).
4. V.E. Tishchenko, ZhRPhKhO 19, 479 (1887).
5. V.E. Tishchenko, ZhRPhKhO 19, 483 (1887); Vech. 20, 704 (1887).
6. M.N. Mladentsev and V.E. Tishchenko. Dmitrii Ivanovich Mendeleev, His Life and Work [in Russian] (Izd. AN SSSR, 1938), Vol. 1.
7. V.E. Tishchenko, ZhRPhKhO 25, 48 (1893).
8. V.E. Tishchenko, Camphor and Terpentine [in Russian] (St. Petersburg, 1895).
9. V.E. Tishchenko, Tr. Keramichesk. inst., No. 9 (1927).
10. V.E. Tishchenko, Aluminum Alkoxides, Their Properties and Reactions [in Russian] (St. Petersburg, 1899).
11. V.E. Tishchenko, ZhRPhKhO 33, 173 (1901).
12. V.E. Tishchenko, Thesis, On the Action of Aluminum Alkoxides on Aldehydes [in Russian] (St. Petersburg, 1906).
13. V.E. Tishchenko, Zap. IRTO, Khim. Otd., 75 (1900).
14. V.E. Tishchenko and A.P. Sidorkina, ZhPKh 8, 1117 (1935).
15. V.E. Tishchenko and A.G. Evdokimov, ZhPKh 4, 640 (1931).
16. V.E. Tishchenko, M.I. Leshkevich and L.A. Skul'skaya, ZhPKh 3, 375 (1930).
17. V.E. Tishchenko and L.I. Antsus, ZhPKh 4, 805 (1931).

18. V.E. Tishchenko and N.V. Koshkin, ZhPKh 7, 1307 (1934).
19. V.E. Tishchenko and V.Ya. Marga, ZhRPhKhO 60, 1009 (1928).
20. V.E. Tishchenko and G.A. Rudakov, ZhPKh 6, 691 (1933); Lesokhim. prom., No. 5-6 (1932); prot. Leningr. otd. VKhO 3, 52 (1934); ZhPKh 7, 37 (1934).
21. V.E. Tishchenko and M.A. Grekhnev, Prom. org. kh. 8, 481 (1937); 11, 238 (1940); ZhPKh 14, 395, 889 (1941).
22. V.E. Tishchenko and A.F. Kosterin, ZhOKh 7, 1366 (1937); B.G. Gavrilov, Thesis, Moscow (1944); V.E. Tishchenko, V.N. Shabashova and N.D. Sysoeva, ZhOKh 10, 1042 (1940).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

STUDY OF THE ALKALINE DECOMPOSITION OF ISOPROPYLBENZENE HYDROPEROXIDE

I. SOME PROPERTIES OF THE HYDRATED SODIUM SALT OF ISOPROPYLBENZENE HYDROPEROXIDE

V.A. Belyaev and M.S. Nemtsov

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3855-3860, December, 1961
Original article submitted January 9, 1961

One of the stages of the industrial process of producing α-methylstyrene via isopropylbenzene hydroperoxide is the decomposition of the latter by the action of a concentrated aqueous solution of caustic soda [1]. However, the mechanism of this reaction has not received an unambiguous explanation up to the present time. Thus, in the first investigations devoted to developing the industrial process, the alkaline decomposition of the isopropylbenzene hydroperoxide was regarded as a two-stage process of the formation of the hydrated salt and its thermal decomposition:

$$ROOH + NaOH + 5H_2O \rightarrow ROONa \cdot 6H_2O$$
$$ROONa \cdot 6H_2O \rightarrow ROH + NaOH + 5H_2O + {}^1/_2O_2$$
$$R = C_6H_5C(CH_3)_2.$$

Kharasch and co-workers [2] ascribed an ionic mechanism to the formation of the main reaction product – dimethyl phenyl carbinol

$$ROOH + NaOH \rightarrow ROO^- + Na^+ + H_2O$$
$$ROO^- + ROOH \rightarrow RO^- + ROH + O_2,$$

which assumes the interaction of the anions of the salt with a molecule of undissociated hydroperoxide. Similar views were expressed again subsequently [3], stress being placed on a chain mechanism of the decomposition of the hydroperoxide with the participation of the RO^- ion.

Ionic notions are somewhat inconsistent with the fact that the rate of alkaline decomposition of the hydroperoxide rises sharply with an increase in the concentration of the aqueous caustic soda solution, the greatest rate being achieved when the water is almost completely eliminated from the reaction system, i.e., when the electrolytic dissociation of the salt is most hampered [1].

In view of this, the properties of the hydrated salt of isopropylbenzene hydroperoxide, forming the initial product according to the hypotheses on the thermal mechanism of the reaction, have been subjected to a more detailed study in the present work.

Since the industrial process of alkaline decomposition of the hydroperoxide consists of introducing an aqueous solution of caustic soda into a solution of the hydroperoxide in isopropylbenzene, the reaction mixture consists of a two-phase heterogeneous system. It was therefore necessary first of all to determine the solubility of the hydrated salt of the hydroperoxide in each of the two phases.

EXPERIMENTAL AND DISCUSSION

The hexahydrate of the sodium salt of isopropylbenzene hydroperoxide was prepared by the interaction of the technical hydroxide (200 g in 200 ml of petroleum ether), cooled to 0°, and a 25% aqueous solution of caustic soda (160 ml). The salt which separated out was washed on a Büchner funnel with the same solution of caustic soda and with petroleum ether. The crystals of the salt were dried in a current of dry nitrogen, after which they were subjected to iodometric analysis [4] and to titration with 0.1 N HCl (with phenolphthalein) to determine the content of ionic sodium. The results of the analyses of the crystals, calculated as the hexahydrate of the sodium salt, are given in

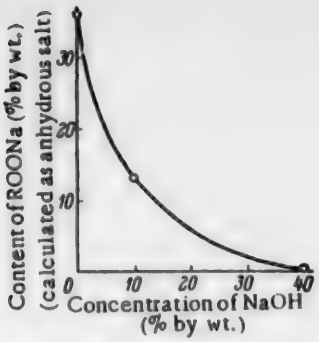


Fig. 1. Solubility of the hexahydrated sodium salt of isopropylbenzene hydroperoxide in aqueous solutions of caustic soda at 20°.

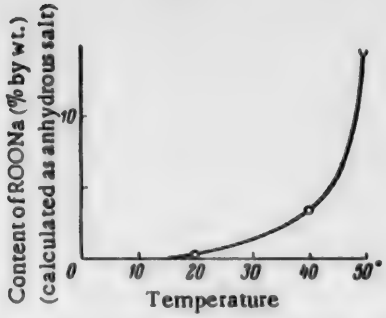


Fig. 2. Solubility of the hexahydrated sodium salt of isopropylbenzene hydroperoxide in isopropylbenzene at various temperatures.

TABLE 1. Chemical Analysis of Crystals of the Hexahydrated Sodium Salt of Isopropylbenzene Hydroperoxide

No. of the sample of crystals	Method of analysis	Content of the salt (in %, calculated as the hexahydrate)
1	Iodometric for hydroperoxide [4]	95.0
2		101.0
3		100.2
1	Titration with 0.1 N HCl for sodium ion	100.8
2		99.5
3		101.0

Table 1, from the data of which it follows that the crystals which separated consist of the practically pure hexahydrated sodium salt of isopropylbenzene hydroperoxide.

These results do not agree with literature indications [5,6] on the formation of tetrahydrate under similar conditions.

The solubility of the hexahydrate was determined in a glass apparatus which consisted of a thermostated test tube with a turbostirrer. The salt was added to the solvent heated to a predetermined temperature, the mixture was stirred intensively for 10 minutes and then the stirrer was stopped and the solution allowed to settle. After complete deposition of the suspension of crystals the transparent solution was sampled for analysis using a thermostated sampler, in the jacket of which water circulated from an ultrathermostated vessel heated to the temperature of the experiment. The analysis of the solution was carried out by the method used for characterizing the initial salt.

Figure 1 gives the data on the solubility of the hexahydrated salt of the hydroperoxide in aqueous solutions of alkali at 20°; they show the sharp diminution in the solubility with an increase in the concentration of alkali. Thus, an increase in the strength of the alkali solution in the two-phase system favors transference of the hydrated salt into the hydrocarbon layer. Figure 2 shows graphically the solubility of the hexahydrate in isopropylbenzene as a function of the temperature, which indicates that the salt, almost insoluble in the cold, has a considerable solubility in isopropylbenzene at high temperatures.

The results obtained show that under the conditions of decomposing isopropylbenzene hydroperoxide with concentrated solutions of alkali at elevated temperatures, the main part of the hexahydrate is present in the hydrocarbon layer. This conclusion is confirmed by visual observations: on adding a 32% aqueous solution of caustic soda to a solution of the hydroperoxide in isopropylbenzene heated to 90-120°, a completely homogeneous mixture is formed.

With respect to the question of the thermal stability of the sodium salt of the hydroperoxide, an examination of the influence of an excess of free hydroperoxide on the rate of decomposition of the salt has considerable interest. In the investigation mentioned [2], it was found that the decomposition of isopropylbenzene hydroperoxide in aqueous solution at 90° and with an excess of alkali goes at a low rate, but with a molar ratio of hydroperoxide to caustic soda of 1:0.2, the reaction velocity rises considerably. From these experiments, the authors of this paper came to the conclusion that, in agreement with the reaction mechanism which the paper posed (see above), the decomposition takes place by means of the interaction of the anion of the salt with free hydroperoxide.

Experiments, the results of which are shown graphically in Fig. 3, were carried out in order to determine quantitatively the interconnection between the rate of decomposition and the ratio of free hydroperoxide and hydroperoxide bound in the form of the salt. The kinetic measurements were carried out in a reaction vessel with a mixer simi-

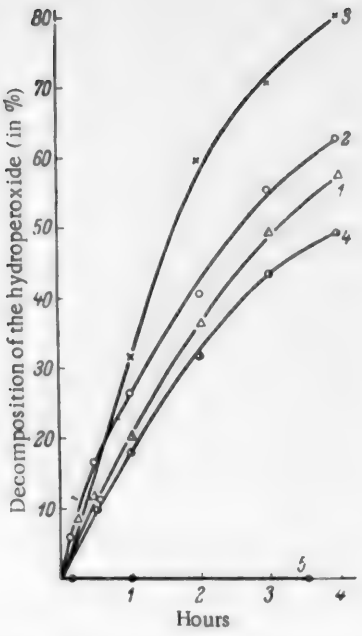


Fig. 3. Rate of decomposition of isopropylbenzene hydroperoxide as a function of the molar ratio between the hydroperoxide and its hexahydrate at 80°. 1) Pure hydrated salt (ROONa · $6H_2O$); 2) ROOH : ROONa $6H_2O$ = 1.17; 3) ROOH : ROONa · $6H_2O$ = 2.1; 4) ROOH : ROONa · $6H_2O$ = 6.3; 5) ROONa · $6H_2O$ at 50°.

lar to the tube for solubility determination described above. Thermostating was carried out by the circulation of heated water from a thermostated reservoir through the jacket. The reaction was carried out in isopropylbenzene solution containing a total amount of the hydroperoxide (free and in the form of sodium salt) equal to 16% by weight. The predetermined ratio between the hydroperoxide and its salt was attained by mixing the hexahydrated salt of the hydroperoxide with pure hydroperoxide obtained from its sodium salt by decomposition with carbon dioxide.

The kinetic curves given in Fig. 3 show that at 80° the greatest reaction velocity corresponds to a molar ratio between the hydroperoxide and the salt of 2 : 1. The pure sodium salt decomposes at a rate almost two times less. Thus, the accelerating influence of the free hydroperoxide on the decomposition proved to be extremely important.

The greatest interest is attached to the data given in Fig. 3 for the pure hexahydrate at 50° (curve 5), when the decomposition practically ceases. This unexpected result, which cannot be explained by the normal slowing down of the reaction (temperature reduction of only 30°), indicated the occurrence of some kind of qualitative changes taking place in the reaction system.

This conclusion agrees with the above-mentioned influence on the reaction velocity of the free hydroperoxide, which apparently reacts with the hexahydrate itself with the formation of some more reactive intermediate products.

To test this hypothesis, the reaction mixture of free hydroperoxide and its hexahydrated salt in isopropylbenzene solutions at a ROOH : ROONa ratio corresponding to the highest reaction velocity was heated to 80° with subsequent rapid cooling ("quenching"). Under these conditions, the precipitation of well-formed crystals having the form of thin transparent plates of regular rectangular form was observed (see photomicrograph in Fig. 4).

From the same mixture, heated only to 50°, on rapid cooling only crystals of a prismatic form, a photomicrograph of which is given in Fig. 5, precipitated.

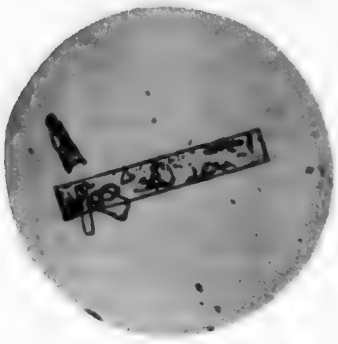


Fig. 4. Photomicrograph of crystals of the trihydrated sodium salt of isopropylbenzene hydroperoxide (×200).

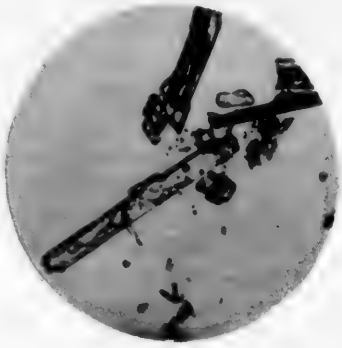


Fig. 5. Photomicrograph of crystals of the hexahydrated sodium salt of isopropylbenzene hydroperoxide (×60).

The results of chemical analysis of the two types of crystals carried out by the method used for the initial salt (see above) are given in Table 2, which shows the values of the molecular weights calculated from the formulas

TABLE 2. Chemical Analysis of Crystals Precipitating from Isopropylbenzene Solutions of a Mixture of the Hexahydrated Salt of Isopropylbenzene Hydroperoxide and the Free Hydroperoxide (molar ratio between the hydroperoxide and the salt 2 : 1)

Sample of crystals	Method of analysis	Number of the samples of crystals	M	n – number of molecules of water in a molecule of the hydrated form of the hydroperoxide salt
Crystals of prismatic form precipitated after heating to 50°	Iodometric	1	284	6.1
		2	288	6.3
	Titration with 0.1 N HCl	1	278	5.8
		2	281	6.0
Crystals of plate-like form precipitated after heating to 80°	Iodometric	3	223	2.7
		4	247	4.0
	Titration with 0.1 N HCl	3	226	2.9
		4	231	3.2

$M = \frac{[\text{weight in grams}] \cdot 2}{[\text{liters of 1 N } Na_2S_2O_3]}$ and $M = \frac{[\text{weight in grams}]}{[\text{liters of 1 N HCl}]}$, respectively.

The last column of Table 2 shows the values of n – the number of molecules of water in a molecule of the hydrated form of the hydroperoxide salt calculated from the formula $n = \frac{M-174}{18}$, where 174 is the molecular weight of the anhydrous salt and 18 is the molecular weight of water.

The data of Table 2 show that the crystals precipitating from the solution previously heated to 50° consist of the practically unchanged hexahydrated salt of the hydroperoxide (M 282).

However, on briefly heating the mixture to 80°, the loss of three molecules of hydrate water takes place with the formation of the trihydrate $ROONa \cdot 3H_2O$ (M 228).

A control experiment in which the hexahydrate was heated to 80° alone under the same conditions led to the precipitation only of crystals of the initial salt. This experiment showed that the thermal dehydration of the hexahydrate does not take place under these conditions in the absence of the free hydroperoxide.

Thus, the results obtained lead to the conclusion that the splitting out of water in the interaction of the hexahydrate with the hydroperoxide takes place by means of a trans-hydration reaction, apparently with the formation of the hydrated form of the free isopropylbenzene hydroperoxide. The existence of the latter was not previously known, but the composition $H_2O_2 \cdot 2H_2O$ has been found for hydrogen peroxide hydrate [7].

From this hypothesis, it is possible to conclude that a similar result will be obtained also on replacing the hydroperoxide by other substances capable of forming hydrates. To test this possibility, experiments were carried out similar to those described above but with the hydroperoxide replaced by dimethyl phenyl carbinol, which is the main product of the alkali decomposition of isopropylbenzene hydroperoxide.

Just as in the experiments with the free hydroperoxide, heating a mixture of the hexahydrate with dimethyl phenyl carbinol (in solution in isopropylbenzene) was carried out at 50 and 80°. Under these conditions, as was to be expected, in the first case only prismatic crystals of the hexahydrate precipitated, and in the second case plate-like crystals of the trihydrate. This result was also confirmed by chemical analyses and calculations of the molecular weights and molecular ratios H_2O : ROONa.

Thus, the trans-solvation reaction of the hexahydrated salt of the hydroperoxide in its reaction with a water-acceptor A may be represented by the scheme

$$ROONa \cdot 6H_2O + nA \rightleftharpoons ROONa \cdot 3H_2O + nA \cdot 3H_2O$$

In order to test the possibility of a further development of the dehydration reaction, i.e., the splitting out of water from the trihydrated sodium salt of isopropylbenzene hydroperoxide, similar experiments were carried out in which isopropylbenzene solutions of a mixture of hydroperoxide with the trihydrate of its salt were heated for a short

time at 80°. On cooling, crystals only of the trihydrate gradually precipitated from the initially transparent solution, their amount at 0° being almost equal to that added initially. However, this result does not exclude the occurrence of the reversible reaction

$$ROONa \cdot 3H_2O + nROOH \rightleftharpoons ROONa + nROOH \cdot 3H_2O,$$

since on subsequent cooling the position of the equilibrium could be displaced in the reverse direction.

In the light of the observations made, the unusual sharp change in the rate of decomposition of the hexahydrated salt of the hydroperoxide with temperature is readily explained: at 50°, when the dehydration of the thermally stable hexahydrate does not take place, the rate of its decomposition is extremely low; at 80°, when the trans-solvation reaction mentioned takes place to a high degree, the decomposition also proceeds at an adequate rate.

From the experiments described, it is still not possible to draw an unambiguous conclusion about what intermediate products determine the rate of the latter reaction. This question will be considered in subsequent communications.

SUMMARY

1. The solubilities of the hexahydrated salt of isopropylbenzene hydroperoxide in isopropylbenzene as a function of the temperature and in aqueous alkali solutions as a function of the concentration of caustic soda have been determined experimentally.

2. A quantitative connection has been shown between the rate of decomposition of isopropylbenzene hydroperoxide and the molar ratio between its sodium salt and free hydroperoxide.

3. It has been found that the hexahydrated sodium salt of isopropylbenzene hydroperoxide undergoes dehydration when it interacts with the free hydroperoxide and with dimethyl phenyl carbinol, the development of this reaction being strongly temperature-dependent.

4. The results obtained allow the abnormally sharp dependence of the rate of decomposition of isopropylbenzene in alkaline solutions on the temperature to be explained.

5. The trihydrated sodium salt of isopropylbenzene hydroperoxide has been isolated in the crystalline state and identified (the salt precipitating from aqueous solutions under normal conditions is the hexahydrate).

LITERATURE CITED

1. M.S. Nemtsov, I.I. Radchenko, S.L. Fisher, Khim. nauka i prom. 2, 306 (1957).
2. M. Kharasch, A. Fono, W. Nudenberg, J. Org. Ch. 17, 207 (1952).
3. C. Tipper, Ind. Chem. 35, No. 3, 113 (1959).
4. Analysis of the Products of the Synthetic Alcohol and Synthetic Rubber Industries [in Russian] VNIISK, 251 (1957).
5. H. Hock, S. Lang, Ber. 77, 257 (1944).
6. United States Patent No. 2,632,026 (1953); Chem. Abs. 48, 2101 (1954).
7. W.C. Schumb, C.N. Satterfield, R.L. Wentworth, Hydrogen Peroxide [translated into Russian] (Moscow, 1958).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

STUDY OF THE ALKALINE DECOMPOSITION OF ISOPROPYLBENZENE HYDROPEROXIDE

II. SOME PROPERTIES OF THE ANHYDROUS SODIUM SALT OF ISOPROPYLBENZENE HYDROPEROXIDE

V. A. Belyaev and M. S. Nemtsov

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3861-3869, December, 1961
Original article submitted January 9, 1961

In the previous paper [1] it was shown that the hexahydrated sodium salt of isopropylbenzene hydroperoxide in admixture with the free hydroperoxide takes part in a trans-solvation reaction, which leads to the formation of the trihydrate. No further dehydration of the hydrates could be achieved under these conditions.

In the present work, attempts have been made to obtain the anhydrous salt of the hydroperoxide by other means. The use of the method of metallation employed for weak acids [2] did not give satisfactory results, since, on the interaction of anhydrous isopropylbenzene hydroperoxide with sodium methoxide and ethoxide, and also with caustic soda, it proved impossible to isolate the salt in the pure form in the cold, and heating led to decomposition of the hydroperoxide. More favorable results were obtained on treating anhydrous isopropylbenzene hydroperoxide with metallic sodium [3]. After a series of preliminary experiments, the following procedure was selected. An air-tight reaction vessel was purged with a current of dry nitrogen and filled with absolute diethyl ether, to which sodium wire was added in a current of dry nitrogen. Then the reaction vessel was cooled to 20-25° below zero and a solution of the hydroperoxide in dry ether was added to it dropwise over 1.5-2 hours. The initial concentration of the hydroperoxide in the reaction liquid was about 10% by vol. When the whole amount of hydroperoxide had been added to the reactor, the latter was connected to a vacuum line of a water-jet pump and the reaction was carried out further with the gradual evaporation of the solvent. In order to separate the reaction products from the excess of metallic sodium and caustic soda, which is formed by side reactions, the contents of the reactor were diluted with n-pentane; the solution was filtered through a No. 1 glass filter and collected in a dry vessel.

TABLE 1. Composition of Some Samples of the "Anhydrous Sodium Salt of Isopropylbenzene Hydroperoxide" Prepared

		Experiment No.		
		I	II	III
Analytical data calculated as ROONa (in % by weight)	a	75.6	70.7	71.3
	b	86.2	80.4	83.6
Calculated contents (in % by weight)	ROONa	75.6	70.7	71.3
	RONa	9.6	8.8	11.2
	ROH	14.8	20.5	17.5

After removing the pentane from the filtrate in vacuum, a viscous transparent liquid remained on the bottom of the vessel; analysis of the liquid by iodometric titration for hydroperoxide [4] indicated that the product contained 70% of the anhydrous sodium salt of the peroxide, while titration for sodium ion with 0.1 N HCl indicated that it contained 80% of the anhydrous salt. The discrepancy between the results is probably due to the fact that the iodometric determination gives the sum of the hydroperoxide salt and the sodium derivative of dimethyl phenyl carbinol, which may be formed by reduction of the hydroperoxide with hydrogen at the moment of its liberation in the main reaction and in the interaction of the carbinol itself with sodium.

TABLE 2. Composition of the Initial Mixtures for Comparing the Rates of Decomposition of the Anhydrous Sodium Salt of Isopropylbenzene Hydroperoxide and its Mixtures with Free Hydroperoxide

		Experiment No.	
		I	II
Basic composition of the initial mixture (in % by weight)	ROONa	7.5	3.9
	ROOH	-	4.2
	RONa	4.15	4.7
	ROH	2.95	3.7
	RH	85.5	83.5
Molar ratio $\frac{ROOH}{ROONa}$		0	1.23
Impurities: Molar ratio $\frac{ROH}{ROONa + ROOH}$		0.50	0.54
Impurities: Molar ratio $\frac{RONa}{ROONa + ROOH}$		0.61	0.60

To check the latter hypothesis, the liquid obtained was repeatedly treated with a 10% aqueous solution of caustic soda until the hydroperoxide was completely eliminated. Under these conditions, the sodium alkoxide must have been decomposed simultaneously with the formation of free dimethyl phenyl carbinol. The residual "oily layer," after drying with calcined sodium sulphate, was analyzed for its content of tertiary alcohol by the hydrochlorination method [4]. The results of the analysis showed that, within the limits of accuracy of the determination, this product consisted of the practically pure carbinol.

Thus, the anhydrous salt obtained was not an individual product but consisted of a mixture containing dimethyl phenyl carbinol and its sodium derivative as impurities. Unfortunately, a direct quantitative determination of all the components of the mixture mentioned is extremely difficult. However, to a degree of approximation its composition may be characterized by the results of chemical analysis for the total content of hydroperoxide and sodium ion.

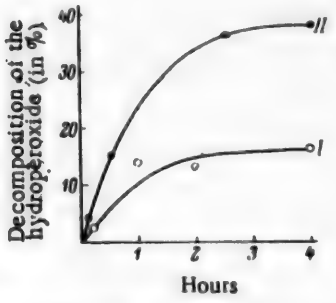


Fig. 1. Comparison of the rates of decomposition of the anhydrous sodium salt of isopropylbenzene hydroperoxide (I) and mixtures of it with the free hydroperoxide (II) in isopropylbenzene at 50° (see Table 2).

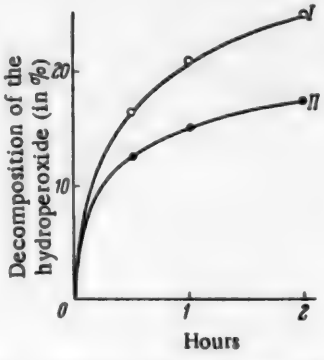


Fig. 2. Effect of the addition of the sodium derivative of dimethyl phenyl carbinol on the degree of decomposition of the sodium salt of the hydroperoxide. I) Initial sodium salt; II) sodium salt with the addition of 25% of alkoxide.

TABLE 3. Chemical Analysis of the Pyramidal Crystals

Sample No.	Number of g-moles in 100 g of substance		Molar ratio $\frac{ROONa + ROOH}{ROONa}$	Content of [ROONa · ROOH] (in % by weight)	
	Content of peroxide oxygen	Content of sodium		From peroxide oxygen	From Na^+
I	0.6060	0.3100	1.95	98.7	101.0
II	0.6050	0.3040	1.98	98.6	99.4
III	0.6125	0.3070	2.00	99.9	100.0
IV	0.6017	0.2935	2.00	98.3	95.4
V	0.6190	0.3110	1.99	101.0	101.4
VI	0.6100	0.3095	1.97	99.6	101.0

Since the process of obtaining the anhydrous salt is carried out with the excess of metallic sodium, it may be assumed that all the hydroperoxide is present in the bound state, i.e., the iodometric determination of the hydroperoxide corresponds to its sodium salt alone, a = % by weight of ROONa. Titration for sodium ion (0.1 N HCl), provisionally calculated also as ROONa, gives a figure b, the value of which permits the content of the sodium derivative of dimethyl phenyl carbinol c to be calculated from the formula c = % by weight RONa = b − a) · $\frac{158}{174}$, where 158 is the molecular weight of the alkoxide and 174 is the molecular weight of the hydroperoxide salt.

Hence, the content of free dimethyl phenyl carbinol in percent by weight amounts to: ROH = 100 − a − c.

The compositions of the individual samples of "anhydrous salt" prepared given in Table 1 were determined in this way.

On the basis of these data, it appeared to be possible to compose mixtures of predetermined composition in subsequent experiments.

In view of the interconnection between the rate of decomposition of isopropylbenzene hydroperoxide and the molar ratio between its hydrated sodium salt and the free hydroperoxide elucidated in the previous paper, similar experiments were carried out in anhydrous systems. The compositions of the initial mixtures were selected in such a way that the content of contaminating dimethyl phenyl carbinol and its sodium derivative, in relation to the total amount of free and combined hydroperoxide (ROOH and ROONa), was practically constant (Table 2).

The kinetic curves obtained for these experiments, given graphically in Fig. 1, show that the addition of the free hydroperoxide to its anhydrous sodium salt at a molar ratio ROOH : ROONa = 1.23 not only increasesthe rate of the reaction but also strongly increases the limiting conversion. These results may be explained in the following manner. In the previous paper [1], it was shown that the hexahydrated sodium salt of the hydroperoxide in solution inisopropylbenzene at 50°, and also the free hydroperoxide [5], undergo practically no decomposition. If it is assumed that the anhydrous salt is equally stable under these conditions, then the addition of the free hydroperoxide will lead to the formation of some reactive intermediate compound which will determine the rate of the reaction. According to this, the existence of a limit to the conversion is a consequence of the practically complete exhaustion of the free hydroperoxide at this moment, when only the heat-stable sodium salt remains in the reaction mixture.

At first sight, this explanation is contrary to the results of experiment 1, where free hydroperoxide was not added and a reaction was nevertheless observed. However, in this case, free hydroperoxide might be formed through an exchange reaction between the hydroperoxide salt and the carbinol by the scheme

$$ROONa + ROH \rightleftharpoons ROOH + RONa. \quad (1)$$

The amount of hydroperoxide formed is determined by the final concentration of free dimethyl phenyl carbinol in the mixture.

From the hypothesis of the occurrence of the reversible exchange reaction (1), it followed that the addition of the sodium derivative of dimethyl phenyl carbinol to the reaction mixture should, by displacing the equilibrium of reaction (1) to the left, reduce the degree of conversion. The results of appropriate experiments given in Fig. 2 confirm this conclusion.

Fig. 3. Photomicrograph of crystals of the complex ROONa · ROOH (× 15).

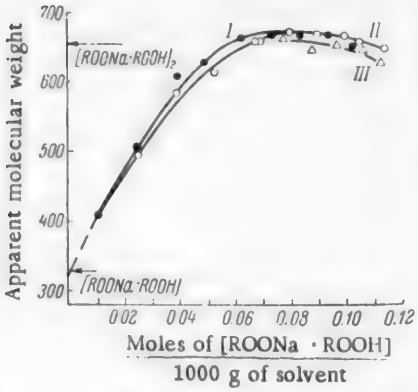


Fig. 4. Cryosocopic measurements of the molecular weight of the complex ROONa ROOH in benzene. I, II, III) Different measurements.

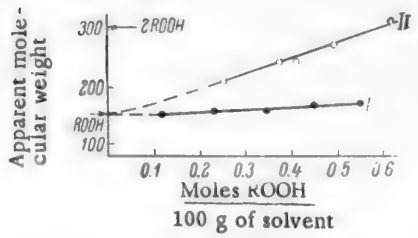


Fig. 5. Cryoscopic measurements of the molecular weight of isopropylbenzene hydroperoxide. I) In benzene; II) in cyclohexane.

In developing the procedure for obtaining the anhydrous sodium salt, the precipitation of a small amount of white flocculent precipitate was noted. The latter was separated, washed with n-pentane, dried in the cold in vacuum in a current of dry nitrogen, and subjected to iodometric analysis for its hydroperoxide content and titrated with 0.1 N HCl to determine its sodium ion content. It was found that the molar ratio of ROOH to $Na^+ \approx 2$. These results enabled it to be assumed that this precipitate consists of a compound of the hydroperoxide with its salt or with the sodium derivative of dimethyl phenyl carbinol. Direct experiments were carried out to test this. On mixing the free hydroperoxide with the sodium derivative of dimethyl phenyl carbinol, no precipitate at all separated. There was also no separation of the precipitate when a large excess of the hydroperoxide was added to the anhydrous salt (2:1). The copious formation of a white crystalline precipitate was successfully achieved when the hydroperoxide and its anhydrous sodium salt were mixed in equimolecular proportions at the temperature of an ice bath, a considerable evolution of heat being observed.

To obtain an individual crystalline product, the following procedure gave satisfactory results. The previously prepared and analyzed anhydrous sodium salt of isopropylbenzene hydroperoxide was placed in a weighed flask purged with dry nitrogen. Under a current of dry nitrogen, the latter was disconnected and reweighed. Then the stoichiometric amount of anhydrous hydroperoxide and pentane in an amount calculated to give a solution containing 50% of the solvent were added to the flask. On cooling this solution in an ice bath, crystals gradually accumulated on the walls of the flask, and after 8-12 days the process of crystallization was completed. The mother liquors were removed with the aid of a syphon and the crystals on the walls of the flask were twice carefully washed with dry ether. The solvent residues were removed by pumping off in vacuum in the cold and subsequently purging the flask with dry nitrogen. The crystals obtained proved to be extremely hygroscopic and readily decomposed in air. However, when they were rapidly removed from the atmosphere of dry nitrogen and placed between two microscope slides, well-formed thick needles of pyrimidal form were found. The photomicrograph of these crystals given in Fig. 3 shows that it was, nevertheless, not possible completely to avoid their decomposition by atmospheric moisture and carbon dioxide. Comparison of this photomicrograph with those given in the previous communication [1] shows that the crystals isolated in the present work differ markedly in their form from the crystals of the trihydrated and hexahydrated sodium salts of the hydroperoxide.

The results of chemical analysis of the samples of crystals given in Table 3 show that, within the limits of accuracy of the determination, the crystalline substance isolated is a compound in which the molar ratio between the amount of active (peroxide) oxygen and sodium ion is two.

It may be assumed from these results that the crystals obtained consist of a complex, the structure of which may be illustrated by the formula $[ROONa \cdot ROOH]_n$. The figures of the last columns of Table 3, calculated from the results of chemical analysis, may serve as a confirmation of the assumption made.

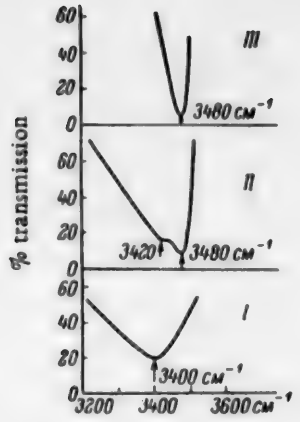


Fig. 6. Infrared spectra of pure isopropylbenzene hydroperoxide in benzene solutions. I) 5 M solution, cell thickness 0.102 mm; II) 1 M solution, cell thickness 0.25 mm; III) 0.1 M solution, cell thickness 4.25 mm.

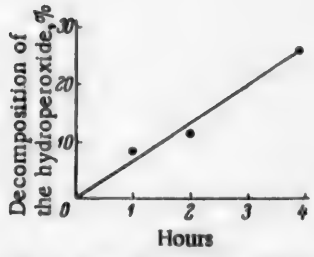


Fig. 8. Rate of decomposition of the complex ROONa · ROOH in carbon tetrachloride at 30°.

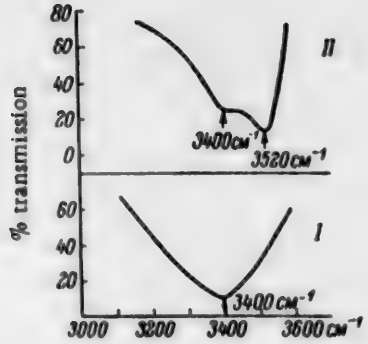


Fig. 7. Infrared spectra of pure isopropyl benzene hydroperoxide in carbon tetrachloride. I) 1 M solution, cell thickness 0.25 mm; II) 0.1 M solution, cell thickness 4.25 mm.

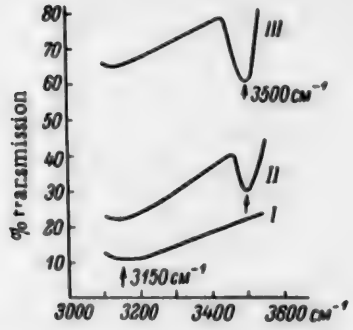


Fig. 9. Infrared spectra of the complex ROONa · ROOH in carbon tetrachloride. I) 0.5 M solution of [ROONa · ROOH] cell thickness 1 mm; II) 0.05 M solution, cell thickness 5 mm; III) 0.01 M solution, cell thickness 5 mm.

To establish the degree of association of the complex, its molecular weight was determined by the cryoscopic method. For this purpose, the crystals were dissolved in dry benzene in a Schlenk apparatus and the solution obtained was transferred to an air-tight cryoscopic apparatus with an electromagnetic stirrer [6]. The determinations were carried out with successive dilutions with the same dry benzene as was used for preparing the initial solution.

The results of the measurements are shown in Fig. 4. The highest molecular weight was found at a concentration of the complex corresponding to 0.08 g-mole of ROONa · ROOH in 1000 g of benzene, practically agreeing with the theoretical value of the molecular weight of the dimer $[ROONa \cdot ROOH]_2$ –652. However, on diluting the solution, the mean value of the molecular weight gradually diminished, reaching the theoretical value for the monomer ROONa · ROOH – 326 – at infinite dilution. A certain reduction in the observed value of the molecular weight at concentrations of the monomer higher than 0.08 g-mole per 1000 g of solvent is obviously due to a deviation from the laws of ideal solutions, increasing with the concentration.

Thus, the experiments described not only confirmed the results of chemical analysis, but also showed the ability of the compound obtained to associate with the formation of a dimer not, apparently undergoing further association.

The measurements described could be distorted if association between the molecules of the free isopropylbenzene hydroperoxide or its salts took place. There is no relevant information in the literature, but association has been observed for other organic hydroperoxides [7]. In view of this, measurements of the molecular weight of solutions of isopropylbenzene hydroperoxide were carried out by the method described. The experimental results obtained, which are illustrated in Fig 5, showed that the hydroperoxide is practically unassociated in very dilute benzene solutions. However, in cyclohexane solution, an increase in the degree of association was observed with a rise in the concentration of the hydroperoxide. Here it is important to note that the increase in the observed molecular weight does not tend to a maximum but rises linearly over the whole range of concentrations investigated. This relationship permits the assumption that the free hydroperoxide, unlike its complex with the sodium salt, forms polymeric associates. The low capacity of the hydroperoxide for association in benzene solutions may, by analogy with the association of alcohols [8], be due to an interaction of the hydroperoxide group with the π-bonds of the benzene [9].

As is known, the association of alcohols takes place by means of intermolecular hydrogen bonds formed between the hydroxyl groups. In accordance with this, the most probable assumption is that the formation of the complex mentioned above is determined by the appearance of hydrogen bonds between the hydrogen of the hydroxyl group of the hydroperoxide and one of the oxygen atoms of its sodium salt. To test this hypothesis, the infrared spectra (IRS) both of the complex ROONa · ROOH itself and of free isopropylbenzene hydroperoxide were taken.* The spectra were taken on the ISK-2 double-beam automatic recording spectrograph with wavelength rectification, using a lithium fluoride prism. The accuracy of the calibration of the apparatus corresponded to an error of 10-15 cm^{-1}.

When a hydrogen bond is present, in addition to the narrow bands of OH group vibrations in the 3500 cm^{-1} region of the infrared spectrum, a broad band displaced toward the lower frequencies is found. This latter band arises from the vibrations of the OH groups taking part in the hydrogen bonding, this band being the more intense and broader, and its displacement to the long-wavelength region being the greater, the stronger the hydrogen bond [9].

The experimental curves obtained for solutions of the hydroperoxide in benzene and carbon tetrachloride and shown in Figs. 6 and 7 give a typical picture of the appearance of a hydrogen bond when the concentration of hydroxyl-containing compounds in solution is changed. Thus, in benzene at a concentration of hydroperoxide of 0.1 M, only a narrow absorption band with a maximum at about 3480 cm^{-1}, characteristic for unassociated OH groups, is found. On increasing the concentration of the solution to 1M, side by side with this band, an absorption band of an associated OH group appears, the maximum of which is displaced to the 3400 cm^{-1} region. At a concentration of 5 M, only this latter band is found, which indicates the practically complete association of the hydroperoxide.

The data obtained from the IR spectra permit some conclusions to be drawn about the evaluation of the energy of the hydrogen bond for the compounds investigated. The displacement of the frequency of the vibrations of the hydroxyl groups when the isopropylbenzene hydroperoxide is associated in carbon tetrachloride is 120 cm^{-1}, which agrees closely with the corresponding value for cyclohexyl hydroperoxide in cyclohexane [10], but is considerably less than the 250 cm^{-1} characteristic for alcohols [11]. From this, it follows that the energy of the hydrogen bond between the hydroperoxide molecules is considerably less than in the case of the association of alcohols.

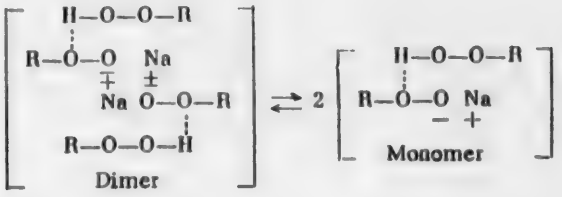
Comparison of the curves in Figs. 6 and 7, reflecting the appearance of a hydrogen bond of the hydroperoxide in dependence on the nature of the solvent, shows that the hydrogen bond in carbon tetrachloride, as was to be expected, is stronger than in benzene solution: the absorption band of the completely associated OH group in the former case appears at a concentration of 1M, while for a benzene solution complete association is achieved only at a concentration of 5 M. This is confirmed also by the fact that the frequency shift in benzene is 40 cm^{-1} less than in carbon tetrachloride.

In the IRS measurements for the complex of the hydroperoxide and its sodium salt, possible errors might arise from the relatively low heat-stability of this compound. In view of the fact that even with a short exposure of the sample in the spectrograph the temperature of the solution under investigation might rise somewhat, it appeared necessary first to check the rate of decomposition of the complex under these conditions. For this purpose, a control experiment was carried out at 30°, the results of which are shown graphically in Fig. 8. Consideration of the kinetic curve given shows that during the 5-10 minutes taken by a measurement, the decomposition of the hydroperoxide does not exceed 1-2%, which cannot seriously affect the results of the spectrographic measurements.

*The authors express their thanks to G. I. Semenov for valuable assistance in taking the infrared spectra.

The IR spectra for solutions of the complex ROONa · ROOH in carbon tetrachloride given in Fig. 9 show that the strength of the hydrogen bond here was considerably greater than for the free hydroperoxide in the same solvent. Thus, while for the latter (Fig. 7) the absorption band of the free OH group is absent for a 1M solution, for the complex this effect was already attained at 0.5 M concentration of ROONa · ROOH. The magnitude of the displacement of the band of the OH group vibrations was found to be 350 cm^{-1} instead of 120 cm^{-1} for the free hydroperoxide. These results permit the conclusion that the energy of the hydrogen bond in solutions of the complex ROONa · ROOH is considerably higher than in all the other cases of intermolecular association through a hydrogen bond studied up to the present time.

The structure of the dimeric complex, from the results obtained, can be represented by the scheme



according to which the monomer is formed by means of an intermolecular hydrogen bond and the dimer by a supplementary dipole association between the heteropolar groups ($\overset{+}{O}\overset{-}{Na}$) of the molecules of the sodium salt of the isopropylbenzene hydroperoxide.

However, the fact that in dilute solutions of the complex of the free hydroperoxide with its sodium salt the IR spectra indicate the presence of free hydroxyl groups allows the possibility of the reversible dissociation of the monomer itself by the following scheme to be assumed:

$$ROONa \cdot ROOH \rightleftharpoons ROONa + ROOH.$$

SUMMARY

1. It has been shown that in anhydrous systems the addition of the free hydroperoxide to its sodium salt increases not only the rate but also the limiting degree of decomposition of the hydroperoxide. The existence of a limit is explained by the exhaustion of the free hydroperoxide and the thermal stability of the sodium salt remaining in the solution.

2. A complex consisting of an equimolecular compound of isopropylbenzene hydroperoxide with its sodium salt has been isolated in crystalline form and identified.

3. It has been shown by cryoscopic measurements that in solution this complex may exist in the form of a monomer and a dimer, forming an equilibrium system

$$2\,[ROONa \cdot ROOH] \rightleftharpoons [ROONa \cdot ROOH]_2.$$

4. Investigation of the infrared spectra of solutions of the complex have shown that the strength of the hydrogen bond in the complex ROONa · ROOH considerably exceeds the strength of the bond characteristic for associates of hydroperoxides and alcohols.

5. The hypothesis has been put forward that the formation of the monomer is due to the appearance of an intermolecular hydrogen bond; and the formation of the dimer, apparently, takes place by dipole association of the heteropolar groups (−ONa) of the molecules of the salt of the hydroperoxide.

LITERATURE CITED

1. V. A. Belyaev, M. S. Nemtsov, ZhOKh 31, 3855 (1961).
2. K. A. Kocheshkov, T. V. Talalaeva, Synthetic Methods in the Field of Organometallic Compounds of Lithium, Sodium, Potassium, Rubidium, and Cesium [in Russian] 172 (Moscow–Leningrad, 1949).
3. M. Kharasch. A. Fono, W. Nudenberg, J. Org. Ch. 17, 207 (1952).

4. Analysis of Products of the Synthetic Alcohols and Synthetic Rubber Industries. VNIISK (Leningrad, 1957).
5. M. Kharasch, A. Fono, W. Nudenberg, J. Org. Ch. 16, 113 (1951).
6. K. Fajans, I. Wurst, Physico-chemical Practice [Russian translation](Leningrad, 1951).
7. A. Rieche. Alkylperoxyde und Ozonide (Dresden –Leipzig, 1931).
8. E. Steurer, K. Wolf. Z. phys. Chem. 39, 101 (1938).
9. N. D. Sokolov, Usp. fiz. nauk 57, 205 (1955).
10. L. Bateman, H. Hughes, J. Chem. Soc. 1952, 4594.
11. V. M. Vol'kenshtein, M. A. El'yashevich, B. I. Stepanov, Vibrations of Molecules. Electroptics of Vibrations of Molecules, Vol. 2 (Moscow, 1949).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. ***Some or all of this periodical literature may well be available in English translation.*** **A complete list of the cover-to-cover English translations appears at the back of this issue.**

POLAROGRAPHY OF DIPHENYLCYCLOPROPENONE

S. I. Zhdanov and M. I. Polievktov

The Institute of Electrochemistry of the Academy of Sciences of the USSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3870-3873, December, 1961
Original article submitted December 19, 1960

In investigations on the polarographic behavior of non-benzenoid aromatic compounds – the tropylium cation [1], pyridinium cyclopentadienylide [2], and azulene [2, 3]–it wasestablished that the presence of a free charge on the part undergoing reduction has a considerable importance not only with respect to the kinetics of the process but in some cases also with respect to its mechanism.

Thus, tropylium cations at a potential of about −0.3 v (normal calomel electrode) undergo one-electron reduction with the subsequent dimerization of the radicals produced to form ditropyl. Apparently the azulenylium cation present in strongly acid solutions of azulene is reduced by the same mechanism [2, 3]. Neutral molecules, namely ditropyl ether – the product of the hydrolysis of tropylium salts – and azulene, are reduced at considerably more negative potentials, the waves and protonic solvents (water, ethanol) corresponding to two-electron transitions. There are reasons for assuming that this phenomenon is widespread in the polarography of organic compounds. Thus, for example, quaternary pyridinium salts are reduced by the same mechanism [4]; pyridine is reduced in the region of more negative potentials and, although the mechanism of its reduction has not yet been definitively established, it is extremely probable that one of its double bonds is reduced. This group of phenomena possibly also comprises the reduction of aromatic aldehydes [5] and tropolone derivatives in acid media in which two one-electron waves are observed. The first wave, apparently, corresponds to the reduction of the protonated molecules, after which the dimerization of the radicals or some other reaction which causes them to disappear may take place, and the second to the two-electron reduction of the neutral molecules.

The reasons for the different mechanism of the reduction of a substance in the ionic form and in the form of neutral molecules consists in the different reduction potentials. According to the rule of electronegativity, the reduction proceeds the more readily the lower the electron density in the molecule or in the electrochemically active group. The considerably greater ease of reduction of cations as compared with neutral molecules is connected just with this factor. It is known that the reduction of hydrocarbons with conjugated double bonds takes place by the scheme

$$R + e \rightarrow \dot{R}^-, \quad (1)$$

$$\dot{R}^- + H^+ \rightarrow \dot{R}H, \quad (2)$$

$$\dot{R}H + e + H^+ \rightarrow RH_2 \quad (3)$$

or

$$2\dot{R}H \rightarrow (RH)_2. \quad (4)$$

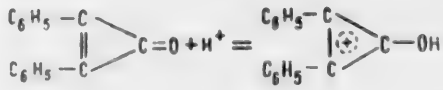
The two-electron wave corresponds to the occurrence of reactions 1-3, and the one-electron wave to the occurrence of reactions 1, 2, and 4. The direction of the process depends on the ratio of the reduction potential of the initial molecule R and the radical $\dot{R}H$. If the radical is reduced more readily than the initial molecule, then at the concentrations studied polarographically, two-electron reduction will be observed.* As the calculations of

*It must be mentioned, however, that at high concentrations of depolarizer the concentration of the radicals $\dot{R}H$ on the surface, in spite of their rapid disappearance by reaction 3, may rise to such an extent that the dimerization reaction 4 begins to complete with reaction 3.

Hoijtink and his co-workers [7] have shown, this situation may occur in the reduction of condensed aromatic systems and polyenes.*

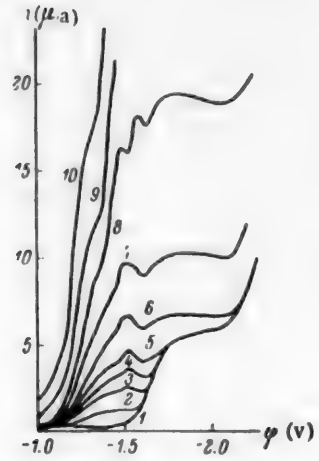
However, if the initial molecule or ion is reduced more readily than the radical which arises, then one-electron reduction takes place. It is obvious that this mechanism exists in the reduction of the cations and protonated molecules mentioned. Further reduction sets in at more negative potentials, at which the occurrence of reaction 3 becomes possible.

In view of what has been said, it was of interest to investigate the polarography of diphenylcyclopropenone, which exists in neutral solutions in the form of neutral molecules, and in acid solutions in the form of cations:



(5)

The single double bond in the three-membered ring of the cation is delocalized, and the cation is a non-benzenoid aromatic hydrocarbon (according to Hückel's rule, the number of π-electrons is $4n + 2$ at $n = 0$).

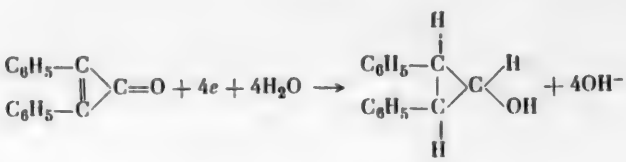


Polarograms of a 10^{-3} M solution of diphenylcyclopropenone in 0.1 M LiCl (50% C_2H_5OH). Concentration of hydrochloric acid (M): 1) 0; 2) $1.98 \cdot 10^{-4}$; 3) $2.96 \cdot 10^{-4}$; 4) $3.92 \cdot 10^{-4}$; 5) $4.88 \cdot 10^{-4}$; 6) $6.76 \cdot 10^{-4}$; 7) 10^{-3}; 8) $1.96 \cdot 10^{-3}$; 9) $5 \cdot 10^{-3}$; 10) 0.1.

In view of the limited solubility of diphenylcyclopropenone in water, the polarography of this compound was studied in aqueous alcoholic solutions containing LiCl and $(C_2H_5)_4NI$.

In neutral solutions of diphenycyclopropenone, two irreversible diffusion waves are observed in $(C_2H_5)_4NI$ with $\varphi_{0.5} = -1.56$ and -1.91 v with respect to the saturated calomel electrode and only the first wave with $\varphi_{0.5} = -1.57$ v in LiCl (figure, curve 1). The limiting current is proportional to the concentration of diphenylcyclopropenone; therefore the waves, particularly the first, may be recommended for use in analysis.

According to the microcoulombometric data, the first wave corresponds to a two-electron process, and the sum of the two waves in $(C_2H_5)_4NI$ to a four-electron process. The four-electron process leads to the reduction of both polarographically active groups in the molecule of diphenylcyclopropenone, i.e., the double bond in the three-membered ring and the carbonyl group.

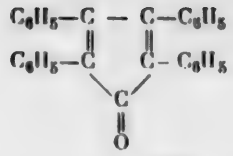


(6)

The product of the reduction of the double bond and the carbonyl group was also obtained by hydrogenating diphenylcyclopropenone over platinum oxide in alcohol and by reduction with lithium aluminum hydride [9].

The first, two-electron, wave may correspond to the reduction of either the double bond or the carbonyl group. The question of which of these two groups is in fact reduced cannot be answered unambiguously from general considerations. For this purpose, an analysis of the reduction products is necessary. There are data in the literature [10] on the analysis of the products of the electrochemical reduction of tetraphenylcyclopentadienone (A), i.e., a compound of closely related structure to diphenylcyclopropenone:

*As a rule, polynuclear condensed aromatic compounds give one-electron waves [8] in consequence of the high conjugation energy, which leads to a marked easing of the reduction of the initial compound and to a high degree of stabilization of the radicals.

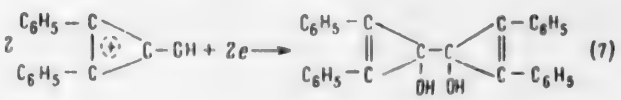


(A)

It was found that in the case of tetraphenylcyclopentadienone, one of the two double bonds in the five-membered ring was reduced first. In the reduction of tropolone by lithium aluminium hydride, a double bond in the ring also undergoes reduction [11]. This gives grounds for assuming that the first wave of diphenylcyclopropenone also corresponds to the reduction of the double bond.

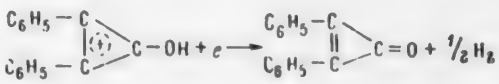
The polarographic behavior of diphenylcyclopropenone in acid solutions is very complex. It can be seen from the figure that on acidifying the solution with hydrochloric acid, one wave still appears, located at lower negative potentials ($\varphi_{0.5} \approx 1.25$ v). The height of this wave is proportional to the concentration of hydrogen ions. It may be assumed that this wave corresponds to the more ready reduction of the cationic form of the compound produced in accordance with reaction 5. In this case, on acidifying the solution, it would increase only to the level of the wave of the initial substance. However, experiment shows that the new wave continues to rise even after it has become equal to the wave in neutral solution (figure). The new wave appearing in acid solutions has a maximum somewhat more sharply expressed at a higher acid concentration. In 0.005 – 0.1 M HCl, already only one wave is found in the polarogram, which increases slightly when the concentration of acid is increased. The limiting current of this wave, has, to all appearances, a mixed diffusion–kinetic character, since the graph of its dependence on the square root of the height of the mercury column is a straight line which does not pass through the origin. Electrolysis of a small volume of the solution at a constant potential corresponding to the limiting current of the wave in strongly acid solutions causes a considerable reduction in the wave, which indicates the presence of a diffusion component in the limiting current.

It is apparently impossible to give an unambiguous interpretation of the phenomena observed on the basis of the polarographic measurements alone. For this purpose, preparative electrolysis with analysis of the products is necessary. It is possible that the wave of diphenylcyclopropenone in acid solutions actually corresponds to the reduction of the cationic form of the compound by the reaction



(7)

with the simultaneous occurrence of the catalytic elimination of hydrogen, for example, by the reaction



(8)

The cations are regenerated by reaction 5.

Thus, in this case also two-electron reduction of neutral molecules takes place and, probably, one-electron reduction of the cations.

The authors thank A. N. Frumkin, M. E. Vol'pin, and S. G. Mairanovskii for valuable advice given during the discussion of the results, and M. E. Vol'pin also for the kind gift of the diphenylcyclopropenone preparation.

SUMMARY

1. The polarography of diphenylcyclopropenone in neutral and acid $(C_2H_5)_4NI$ and LiCl media has been studied.

2. In neutral solutions, diphenylcyclopropenone gives either a single wave of the reduction of the double bond in the ring with $\varphi_{0.5} = -1.56$ (in LiCl), or, in addition to this wave, a wave of the reduction of the carbonyl group with $\varphi_{0.5} = -1.9$ v.

3. On acidifying the solution, a wave with $\varphi_{0.5} = 1.25$ v appears, which has a diffusion character in weakly acid solutions and a mixed diffusion – kinetic character in strongly acid solutions (0.1 N HCl). This wave apparently corresponds to the simultaneous occurrence of the one-electron reduction of the cationic form of diphenyl cyclopropenone with the subsequent dimerization of the radicals and the catalytic elimination of hydrogen.

LITERATURE CITED

1. M. E. Vol'pin, S. I. Zhdanov, D. N. Kursanov, DAN SSSR 112, 264 (1959); S. I. Zhdanov, Z. phys. Ch. (DDR), Sonderheft, 235 (1958); S. I. Zhdanov, A. M. Frumkin, DAN SSSR 122, 412 (1958).
2. S. I. Zhdanov, L. S. Mirkin, Coll. Cz. Chem. Commun. 26, 370 (1961).
3. L. H. Chopard - Dit - Jean, E. Heilbronner, Helv. Chim. Acta 36, 144 (1953); P. Zuman, Z. phys. Ch. (DDR), Sonderheft, 243 (1958).
4. S. G. Mairanovskii, Proceedings of the 4th Electrochemical Congress [in Russian] Izd. AN SSSR, 223 (1959).
5. I. A. Korshunov, L. N. Sazanova, ZhFKh 23, 1299 (1949).
6. J. C. James, J. C. Speakman, Trans. Farad. Soc. 48, 474 (1952); W. J. Neish, O. H. Müller, Rec. trav. chim. 72, 301 (1953); F. Santavý, Coll. Cz. Chem. Commun. 14, 145 (1949).
7. G. J. Hoijtink, J. van Schooten, Rec. trav. chim. 71, 1089 (1952); 72, 691 (1953).
8. J. Bermann, Trans. Farad. Soc. 50, 829 (1954).
9. D. N. Kursanov, M. E. Vol'pin, Yu. D. Koreshkov, ZhOKh 30, 2877 (1960).
10. P. H. Given, M. E. Peover, J. Chem. Soc. 1960, 465.
11. V. Michovich, M. Mikhailovich, Lithium Aluminium Hydride and its Use in Organic Chemistry [in Russian] IL (1957).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

POLAROGRAPHY OF DIETHYLAMINOETHYLMERCAPTAN

S. I. Zhdanov

The Institute of Electrochemistry of the Academy of Sciences of the USSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3874-3877, December, 1961
Original article submitted December 19, 1960

A paper [1] has been devoted to the polarography of mercaptans in which it was shown that alkyl mercaptans give two anode waves, of which the first in 85-90% ethanol 0.025 N with respect to sulfuric acid has $\varphi_{0.5} = +0.02$ V and a limiting diffusion current proportional to the concentration of the mercaptans. The second mercaptan wave was not well reproducible. The author of the paper mentioned notes that the composition of the solution and the pH have some effect on the half-wave potential. The anode wave of mercaptans is ascribed to the process

$$RSH + Hg \longrightarrow RSHg + H^+ + e. \quad (1)$$

It is known that the anode waves corresponding to the formation of insoluble mercury compounds are accompanied by preliminary absorption waves which correspond to the greater ease of occurrence of the process in consequence of the gain of energy on absorption of the reaction product [2] or the inhibition of the process by a film of insoluble products [3]. The absence of absorption waves in the case of the oxidation of mercaptans appeared inexplicable.

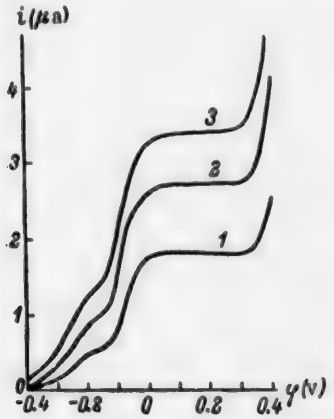


Fig. 1. Polarogram of a 5.6 $\times 10^{-4}$ M aqueous solution of $(C_2H_5)_2NCH_2CH_2SH$ in 0.1 M $(NH_4)_2SO_4$ (curves corrected for residual current). Values of h (in cm Hg): 1) 20; 2) 40; 3) 60.

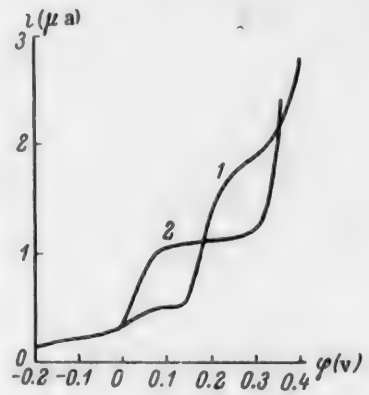


Fig. 2. Polarograms of a 4.8×10^{-4} M ethanolic solution of $(C_2H_5)_2NCH_2CH_2SH$. 1) In 0.1 M $NaClO_4$ (20 ml); 2) in the same solution with the addition of 0.1 ml of conc. $HClO_4$.

The polarograms of diethylaminoethylmercaptan $(C_2H_5)_2NCH_2CH_2SH$ were recorded on the PÉ-312 electronic polarograph in 0.1 M aqueous solutions of $(NH_4)_2SO_4$ and in 0.1 M ethanolic solutions of $NaClO_4$. The capillary had the following characteristics: m = 2.66 mg/sec, and τ = 2.86 sec.

In aqueous (Fig. 1) and ethanolic (Fig. 2) solutions, diethylaminoethylmercaptan gives two anode waves on the polarogram. The height of the first wave, beginning at approximately 2×10^{-4} M, does not depend on the concen-

tration of the mercaptan and is proportional to the height of the mercury column. When the temperature is raised to 65°, the wave disappears. These properties of the wave indicate its absorption character. The second wave, located at more positive potentials, is a diffusion wave, since the limiting current is proportional to the concentration of mercaptan and to the square root of the height of the mercury column and gradually rises with an increase in the temperature (temperature coefficient of the order of 1.5% per degree).

The half-wave potentials of the first and second waves in various media are given in the table.

Half-Wave Potentials of Diethylaminoethylmercaptan in Neutral Aqueous and Alcoholic Solutions

Composition of the solution	$\varphi_{0.5}$ (v)	
	1st wave	2nd wave
0.1 M. $NaClO_4$ + 0.48 · 10^{-3} M $(C_2H_5)_2NCH_2CH_2SH$ (Ethanolic solution)	0	+0.17
0.1 M. $(NH_4)_2SO_4$ + 1.6 · 10^{-3} M $(C_2H_5)_2NCH_2CH_2SH$ (Aqueous solution)	−0.12	+0.04
0.1 M $(NH_4)_2SO_4$ + 5.6 · 10^{-4} M $(C_2H_5)_2NCH_2CH_2SH$ (Aqueous solution)	−0.25	−0.1

Note: The values of the potentials are given with respect to the saturated calomel electrode.

It can be seen from the data of the table that the waves of the mercaptan are located at more positive values of the potential in ethanolic solutions than in aqueous solutions, in consequence of which the area of the limiting current in ethanolic solutions is smaller (Fig. 2) than in aqueous solutions (Fig. 1).

The limiting diffusion current of a 10^{-3} M solution of the mercaptan in ethanol with the given characteristics of the capillary is 2.68 μa per 1 mole. This magnitude corresponds to a one-electron process. Actually, calculation from Il'kovich's equation led to the following values for the diffusion coefficient: at n = 1, D = 3.76 · 10^{-6} cm^2/sec; at n = 2, D = 0.94 · 10^{-6} cm^2/sec; at n = 3, D = 0.42 · 10^{-6} cm^2/sec.

Of the three values of the diffusion coefficient, the first, calculated with the assumption that n = 1, seems the most probable. Since the viscosity of ethanol is 20% higher than the viscosity of water, the diffusion coefficient of diethylaminoethylmercaptan in aqueous solution (n = 1) is approximately 4.5 · 10^{-6} cm^2/sec.

The adsorption wave appears as a result of the adsorption of the reaction product on the mercury:

$$(C_2H_5)_2NCH_2CH_2SH + Hg \longrightarrow (C_2H_5)_2NCH_2CH_2SHg + H^+ + e. \qquad (2)$$

Where the adsorption waves appear before the waves of the reversible process, the magnitude of the limiting adsorption current may be used to calculate the surface of the mercury occupied by one molecule of reaction product [2]. The following data show the reversible nature of the process in the oxidation of diethylaminoethylmercaptan: 1) the adsorption wave disappears with a rise in the temperature; 2) the adsorption wave is considerably lower in ethanolic solution (0.26 μa) than in aqueous solution (0.55 μa); apparently the adsorption of ethanol as the solvent considerably diminishes the adsorption of the reaction product. Hence, the surface occupied by one molecule of reaction product must be calculated from the limiting current of the adsorption wave in aqueous solution; 3) the slope of the diffusion waves of the mercaptan (75 mv in ethanolic and 68 mv in aqueous solution) does not markedly differ from the slope of the reversible one-electron wave (59 mv).

The current strength of 0.55 μa or 0.55 μcoulomb/sec corresponds to the formation of $\frac{0.55 \cdot 10^{-6} \cdot 6.02 \cdot 10^{23}}{96500}$ = 3.43 · 10^{12} molecules of the reaction product per second. The area of mercury surface exposed per second is calculated from the equation [4]: $q = 0.0085 \cdot \frac{m^{2/3}}{\tau^{1/3}} = 0.0085 \frac{(2.66)^{2/3}}{(2.86)^{1/3}}$ = 0.0115 cm^2/sec = 1.15 · 10^{14} A^2/sec. For each molecule of reaction product there is 1.15 · 10^{14}/3.43 · 10^{12} = 33.5 A^2.

Thus, the experimental results indicate that the adsorption wave of diethylaminoethylmercaptan is a wave of the type of Brdička's adsorption waves, i.e. a wave preceding a reversible wave. Adsorption waves preceding waves of irreversible processes have different properties, and calculation of the surface occupied by one molecule of reaction product leads to figures which are too low [5].

An interesting phenomenon is observed on acidifying a neutral solution of diethylaminoethylmercaptan (Fig. 2, curve 2). On adding acid in an amount equivalent to the amount of mercaptan, the diffusion wave diminishes by a factor of almost two and shifts in the negative direction to such an extent that it occupies the place of the adsorption wave, which disappears. The reduction in the height of the wave must obviously be due to a change in the diffusion coefficient of the mercaptan on acidifying the solution in consequence of the protonization of the amino group, accompanied by the pronounced solvation of the molecule and its straightening.

As regards the displacement of the wave in the negative direction, i.e., the facilitation of the process in acid solutions, this phenomenon is also connected with a change in the state of the molecule of diethylaminoethylmercaptan on acidifying the solution.

Let us consider the oxidation of the mercaptan in more detail. Two mechanisms for the process may exist with different initial elementary electron-removal processes.

$$\text{I}\begin{cases}(C_2H_5)_2NCH_2CH_2SH \rightleftarrows (C_2H_5)_2NCH_2CH_2\dot{S} + H^+ + e & (3)\\ (C_2H_5)_2NCH_2CH_2\dot{S} + Hg \longrightarrow (C_2H_5)_2NCH_2CH_2SHg & (4)\end{cases}$$

$$\text{II}\begin{cases}Hg \rightleftarrows Hg^+ + e & (5)\\ (C_2H_5)_2NCH_2CH_2SH + Hg^+ \longrightarrow (C_2H_5)_2NCH_2CH_2SHg + H^+ & (6)\end{cases}$$

It has been shown above that the process, in the main, takes place reversibly. This means that the two stages must occur fairly rapidly. According to a general rule [6], the removal of a proton with a labile bond takes place reversibly. Reaction (3) satisfies this condition. It is extremely probable that reaction (4) following it also takes place rapidly, i.e., at a higher rate than the second stage of the second mechanism (reaction 6). Thus, from general considerations the first mechanism must be considered preferable.

The change of state of the diethylaminoethylmercaptan molecules on acidifying the solution apparently consists in the rupture of a hydrogen bond between the nitrogen and sulphur atoms. The possibility of the formation of a hydrogen bond in the molecule of diethylaminoethylmercaptan follows from the fact that the nitrogen atom possesses a free electron pair and the hydrogen atom connected to the sulphur is labile. As can be seen from Fig. 3, which shows the skeleton of the molecule constructed on the assumption that it is coplanar with the known interatomic distances and bond angles, the appearance of a hydrogen bond is fully allowable, even if the coplanarity of the molecule is not observed strictly. With a plane molecular structure, the S–N distance is 2.7 A and 2.7 A - 1.35 A = 1.35 A remains for a hydrogen bond. Hydrogen bonds occur at distances of 1.6 - 2.0 A [7].

It must be assumed that the removal of a proton (reaction 3) from the thiol group of the molecule of diethylaminoethylmercaptan with a hydrogen bond (in neutral solutions) takes place with somewhat greater difficulty than from a free thiol group (in acid solutions).

The phenomenon observed is less probable on the basis of the mechanism of process II (reactions 5 and 6).

The absence of an adsorption wave in the polarograms of acid solutions of the mercaptan is probably due to the fact that, under these conditions, the reaction product, like the initial substance, is protonated, i.e. there is a positive charge, in consequence of which its adsorption on the positively charged surface of the mercury becomes impossible.

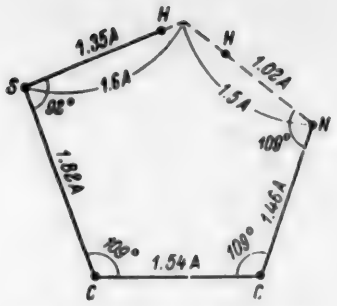


Fig. 3. Skeleton of the molecule of $(C_2H_5)_2NCH_2CH_2SH$ (showing also the direction of the nitrogen valency and the distance of a hydrogen atom connected to it covalently).

SUMMARY

1. The polarography of diethylaminoethylmercaptan has been studied in neutral and acid aqueous and aqueous-ethanolic $NaClO_4$ and $(NH_4)_2SO_4$ solutions.

2. It has been established that in neutral solutions diethylaminoethylmercaptan gives two anode waves. The first wave has an adsorption character and is due to the adsorption on the electrode of the reaction product: $(C_2H_5)_2NCH_2CH_2SHg$. The second wave is a diffusion wave.

3. It has been shown that when the solution is acidified the adsorption wave disappears and the diffusion wave is displaced in the direction of less negative potentials. This phenomenon is due to the rupture of a hydrogen bond between the nitrogen and sulphur atoms when the amino group is protonated.

LITERATURE CITED

1. M. I. Gerber, ZhAKh 2, 265 (1947).
2. R. Brdička, Coll. Cz. Chem. Commun. 12, 522 (1947).
3. I. M. Kolthoff, C. S. Miller, J. Am. Chem. Soc. 63, 1405, 2732 (1941).
4. I. M. Kolthoff, J. J. Lincane, Polarography [Russian translation] Goskhimizdat, 119 (1948).
5. S. I. Zhdanov, A. N. Frumkin, DAN SSSR 122, 412 (1958).
6. Z. R. Grabowski, Prace Konferencji polarograficznej, Warszawa, 91 (1956); M. von Stackelberg, P. Weber, Z. Elektroch. 56, 806 (1952); M. von Stackelberg, Elektrochemische Potentiale organischer Stoffe. 1 In the book: E. Muller, Methoden der organischer Chemie, B. III, Tl. 2, Stuttgart (1955).
7. Ya. K. Syrkin, M. E. Dyatkina, The Chemical Bond and Molecular Structure [in Russian] Goskhimizdat, 327 (1946).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

INVESTIGATION OF THE HYDROLYSIS OF SALTS OF METHYL SULFURIC AND ETHYL SULFURIC ACIDS BY THE ISOTOPE METHOD

I. P. Grazerov and A. M. Tarasenko

The L. V. Pisarzhevskii Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 3878-3880, December, 1961
Original article submitted January 13, 1961

In the single investigation [1] of the hydrolysis of the acid esters of sulfuric acid using O_{18}, it was shown that the acid esters of the steroid series hydrolyzed in organic solvents by an acyl-oxygen mechanism. Of course, it is impossible to apply the results of this work directly to alkyl esters in an aqueous medium. Of acid esters of other acids, the acid phosphates have been investigated similarly, using the isotope and kinetic method, and it was found that ions of the type $ROPO_3H^-$ hydrolyze by the acyl-oxygen mechanism and do so considerably faster than the $ROPO_3H_2$ molecules, which hydrolyze by an alkyl-oxygen mechanism [2, 3]. In contradistinction to this, $(CH_3O)_2PO_2H$ molecules hydrolyze by the alkyl-oxygen mechanism considerably faster than $(CH_3O)_2PO_2^-$ ions by the acyl-oxygen mechanism. In a strongly alkaline medium, however, these ions hydrolyze very slowly by an alkyl-oxygen mechanism [4].

In the present work, the hydrolysis of salts of methyl and ethyl sulfuric acids was studied in heavy-oxygen water H_2O^{18} or in 1 N solutions of HCl or NaOH in H_2O^{18}. In agreement with the cited paper [1], and also with a paper [5] in which optically active alcohols and a kinetic method were used to investigate the mechanism of the formation of acid sulphates, we have found that the hydrolysis goes by the alkyl-oxygen mechanism.

$$RO{-}SO_3^- + H{-}O^{18}H \longrightarrow ROH + HO^{18}SO_3^-$$

Dostrovsky et al. [6] found that on alkaline hydrolysis of diethyl sulfate the alcohol formed contains less O^{18} than the hydrolyzing alkali. This observation was explained by the parallel occurrence of the reaction by the two mechanisms – the alkyl- and acyl-oxygen mechanisms. In paper [7], the reduced content of O^{18} in the alcohol is explained by the dilution of the heavy oxygen in the hydrolyzing light water in consequence of an exchange with the $>SO_2$ residue of the dialkyl sulfate. In the light of the results of the present work, the observation considered can also be explained by the fact that the hydrolysis partially involves the second alkyl group, giving the light alcohol by the acyl-oxygen mechanism.

On carrying out the hydrolysis of the second alkyl group of the dialkyl sulfates to completion, we found that the alcohol formed has the same isotopic composition as was to be expected in the hydrolysis of one alkyl residue by the alkyl-oxygen mechanism and the other by the acyl-oxygen mechanism, with the assumption of the complete exchange of the oxygen of the $>SO_2$ group with the water.

We also found that under the conditions having preparative importance for the production of heavy-oxygen alcohols, i. e., when a small amount of H_2O^{18} and considerable concentrations of alkali were used, the hydrolysis cannot be carried out in such a way that it reaches only the stage of the formation of the acid ester. The alcohol is formed simultaneously from the two alkyl groups in equal amounts and therefore contains considerably less O^{18} than the hydrolyzing water. In spite of this deficiency, the alkaline hydrolysis of dimethyl and diethyl sulfates is suitable as a preparative method for obtaining $CH_3O^{18}H$ and $CH_3O^{16}H$ by virtue of the good yields and the simplicity and ease of carrying it out on the large laboratory scale.

EXPERIMENTAL

Reactants. The sodium salts of ethyl sulfuric and methyl sulfuric acids and the ammonium salt of ethyl sulfuric acid were obtained by the method of reference [8]. The ammonium salt was twice recrystallized from alcohol and had m.p. 97-98°. The dimethyl sulfate and diethyl sulfate were distilled in vacuum and had b.p. 66-66.3° (10 mm) and 93° (15 mm), respectively.

The neutral, acid, and alkaline hydrolysis of ammonium ethyl sulfate. A mixture of 10 g of the salt and 5.8 g of H_2O^{18} (with a 2.5% excess of O^{18}) was heated in a Favorskii flask for 20 minutes to gentle boiling and then the alcohol was slowly distilled off. The fraction passing over at 78-83° (3.7 g) was boiled with 1 g of anhydrous potash and redistilled. The yield of alcohol with b.p. 78-79° was 3.3 g. To eliminate the dissolved heavy-oxygen water, it was shaken three times with 1 ml of saturated aqueous potash, dehydrated with metallic sodium and again distilled. The product obtained did not contain an excess of O^{18}.

Samples of alcohol obtained under similar conditions but where the water for hydrolysis was replaced by 1 N solutions of hydrochloric acid or caustic soda in H_2O^{18} also contained no excess of heavy oxygen.

Neutral hydrolysis of the sodium salts of ethyl sulfuric acid and methyl sulfuric acid. The ethyl alcohol obtained from 18.4 g of $C_2H_5OSO_3Na \cdot 2H_2O$ and 5.8 g of H_2O^{18} (1% excess of O^{18}), and the methyl alcohol obtained from 11.8 g of CH_3OSO_3Na and 5 g of H_2O^{18} (1% excess of O^{18}), by the method described above did not contain an excess of heavy oxygen.

Complete hydrolysis of dimethyl sulfate. The addition of 126 g (1 g-mole) of dimethyl sulfate to a solution of alkali obtained from 23 g (1 g-atom) of sodium and 78 g of H_2O^{18} (1.2% excess of O^{18}) heated to boiling in a flask provided with a stirrer, a reflux condenser, and a dropping funnel was carried out at such a rate that the boiling was not too violent. The liquid was then heated and stirred for a further 0.5hr. and slowly distilled with a fractionating column. The fraction boiling in the range 63-97.5° was dried with potash and redistilled. The yield of alcohol with b.p. 64-68° was about 45 g. It was dehydrated with metallic sodium. The excess content of O^{18} was 0.38 atoms-% (calculated for the formation of alcohol by the alkyl-oxygen and by the acyl-oxygen mechanism, taking exchange with the $> SO_2$ group into account: 0.40 atoms-%).

Complete hydrolysis of diethyl sulfate. A solution of alkali obtained from 12.2 g (0.53 g-atoms) of metallic sodium and 41 g of H_2O^{18} (1.2% excess of O^{18}) and 82 g (0.53 mole) of diethyl sulfate was boiled and stirred for 2.5 hours in a flask provided with a reflux condenser and a stirrer. The mixture, which no longer contained diethyl sulfate, was distilled with a fractionating column. The fraction with b.p. 75-96° was dried with potash and redistilled. The yield of alcohol with b.p. 77-79° was about 35 g. After dehydration with metallic sodium, the excess content of O^{18} was 0.39 atoms-% (calculated for the formation of alcohol by the alkyl-oxygen and by the acyl-oxygen mechanism, taking exchange with the $> SO_2$ group into account: 0.40 atoms-%).

Stepwise hydrolysis of dimethyl sulfate. The addition of 63 g (0.5 mole) of dimethyl sulfate to a solution of alkali obtained from 11.5 g (0.5 g-atoms) of metallic sodium and 50 g of H_2O^{18} (1.2% excess of O^{18}) contained in a flask fitted with a stirrer, dropping funnel, and fractionating column, and heated in a bath to 80-100°, was carried out over 2 hours with stirring. Under these conditions, 5.7 g of methyl alcohol with b.p. about 65° (fraction 1) was distilled off. Then the bath temperature was raised to 120-130° and a further 7.5 g of alcohol distilled over at 65-67° (fraction 2). Finally, at 140-150°, 13.7 g of a liquid with b.p. 67-97° (fraction 3) and 22 g of water distilled over. Fractions 1,2, and 3, after drying with potash and distillation, gave, respectively, 4.3, 6.1, and 9.3 g of alcohol with b.p. 65-66° (760 mm). The excess contents of O^{18} in the three samples were 0.60, 0.49, and 0.27 atoms-%, respectively.

The isotopic analysis of the alcohols was performed using platinum tubes [9].

SUMMARY

1. The hydrolysis of salts of methyl sulfuric and ethyl sulfuric acids by means of H_2O^{18} or 1 N solutions of acid or alkali in H_2O^{18} proceeds by an acyl-oxygen mechanism.

2. In the action of aqueous alkali on dimethyl sulfate and diethyl sulfate, the first alkyl residue is hydrolyzed by the alkyl-oxygen mechanism and the second by the acyl-oxygen mechanism, and the $> SO_2$ group exchanges oxygen with the water. The heavy-oxygen alcohols produced therefore contain less than half the excess of O^{18} initially in the water. This method for their production is suitable for preparative purposes.

LITERATURE CITED

1. S. Burstein a. S. Lieberman, J. Am. Chem. Soc. 80, 5235 (1958).
2. C. A. Bunton, D. R. Ilewellyn, K. G. Oldham a. C. A. Vernon, J. Chem. Soc. 1958, 3574, 3588.
3. W. W. Butcher a. F. H. Westheimer, J. Am. Chem. Soc. 77, 2420 (1955); J. Kumamoto a. F. H. Westheimer, J. Am. Chem. Soc. 77, 2515 (1955).
4. C. A. Bunton, M. M. Mhala, K. G. Oldham a. C. A. Vernon, J. Chem. Soc. 1960, 3293.
5. N. C. Deno a. M. S. Newman, J. Am. Chem. Soc. 72, 3852 (1950).
6. M. Anbar, I. Dostrovskii, D. Samuel a. A. D. Ioffe, J. Chem. Soc. 1954, 3603.
7. D. N. Kursanov and R. V. Kudryavtsev, ZhOKh 26, 2987 (1956).
8. J. Houben, Die Methoden der organischen Chemie [Russian translation] Vol. 3, No. 1, 188 (1934).
9. I. P. Gragerov, Symposium: "Problem of Kinetics and Catalysis", IX. Isotopes in Catalysis [in Russian], 373 (1957).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

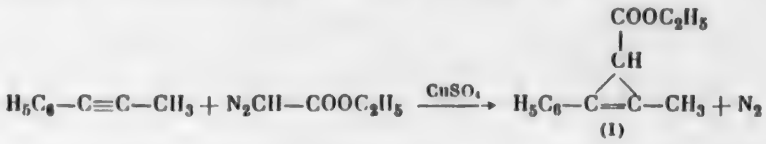
REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

XX. INVESTIGATION OF THE REACTION OF ETHYL DIAZOACETATE WITH 1-PHENYLPROPYNE IN THE PRESENCE OF COPPER SULFATE

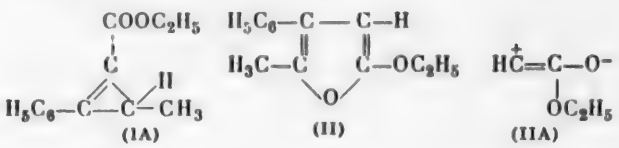
I. A. D'yakonov and M. I. Komendantov

Leningrad State University
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 3881-3893, December, 1961
Original article submitted October 2, 1960

In 1956, we made an attempt to obtain the cyclopropene derivative (I) by the action of diazoacetic ester on the acetylenic hydrocarbon 1-phenylpropyne in the presence of copper sulfate as catalyst [1].



At that time, there was no information whatsoever in the literature on reactions with the liberation of nitrogen between aliphatic diazo compounds and acetylenic hydrocarbons. There were also no data on the reactions of acetylenes with other sources of carbenes. After the short communication [1] on the results of our first attempt in this field had been published, work was continued both in the direction of studying the given reaction and in the direction of carrying out analogous reactions with other acetylenic hydrocarbons – diphenylacetylene [2], oct-4-yne and dec-5-yne [3]. As a result of these investigations, it became clear [3] that when the reaction was carried out in the absence of the copper sulfate and at a higher temperature (necessary to accomplish the thermal decomposition of the diazoacetic ester) derivatives of cyclopropene (I) are formed, while on carrying out the same reaction in the presence of copper sulfate and at a relatively low temperature compounds isomeric with them having different properties, or (at low concentrations of the catalyst) a mixture of these compounds with (I), are formed. From the results of oxidation of the isomeric compounds (with molecular oxygen, ozone, and lead tetraacetate), and also their hydrolytic decomposition in an acid medium, they were assigned the structure of cyclopropenes (IA), distinguished from (I) by the position of the endocyclic double bond.



The following observations [3] were in opposition to this assertion: the unusual stability of the esters of type (IA) to the action of alkalis and the absence of a carbonyl bond in the expected position in the IR absorption spectra of these compounds. It was also found that the esters of type (I) do not isomerize under the action of copper sulfate (under the conditions observed for this reaction) into esters of the (IA) type. The structure of the type (I) esters did not give rise to doubt; it was unambiguously decided from the results of oxidation with potassium permanganate, except, however, for the very ester (I) described in the first communication [1] (see below).

Beginning in 1957 [4], Breslow has obtained cyclopropene derivatives by the same method – i.e., starting from an acetylenic hydrocarbon and an aliphatic diazo compound. However, in contrast to us, he did not use copper sulfate as catalyst but, as has become clear from his subsequent papers, copper bronze [5]. Under these conditions,

compounds of type (I), the structure of which was readily determined by oxidation, were obtained exclusively. As regards the ester (I) described in 1956, although from the data of catalytic hydrogenation it was possible to deduce the presence of a three-membered ring in it [1], the question of the position of the intracyclic double bond remained undecided. Oxidation and ozonization gave no unambiguous answer to the question.

A subsequent study has shown that the careful repeated vacuum distillation of the product under investigation leads to the isolation of a fraction of a substance corresponding in composition to formula (I) but having physical constants different from the constants given in the previous communication. Hence, it was concluded that the condensation product described in this communication, in spite of the satisfactory analytical data, was not free from some impurity or other. The corrected constants were published in 1959 [2] and the condensation product was provisionally assigned [3] formula (IA).

As will be seen from what is said below (see also [6]), the condensation product possessing these constants in fact is not a cyclopropene derivative, but a furane derivative, and has formula (II). As regards the reaction product described in the preliminary communication, according to our data it consists of a mixture of (I) and (II), from which "pure" (II) can be isolated by repeated fractionation. A future paper of this series must be devoted to a description of the method for obtaining "pure" (I).

The idea that the compounds which we investigated, obtained under conditions of catalysis by copper sulfate of the reaction of diazoacetic ester with acetylenes, were furanes and not the isomeric cyclopropenes was first put forward by Breslow and Chipman [7]. The supplementary experimental check of this assertion recently undertaken by us confirmed it completely [6]. At the present time, it must be considered as demonstrated that compounds of type (I) may also be obtained as impurities under the conditions of the copper sulfate catalyzed reaction, the amount of this impurity being in inverse dependence on the amount of catalyst taken.

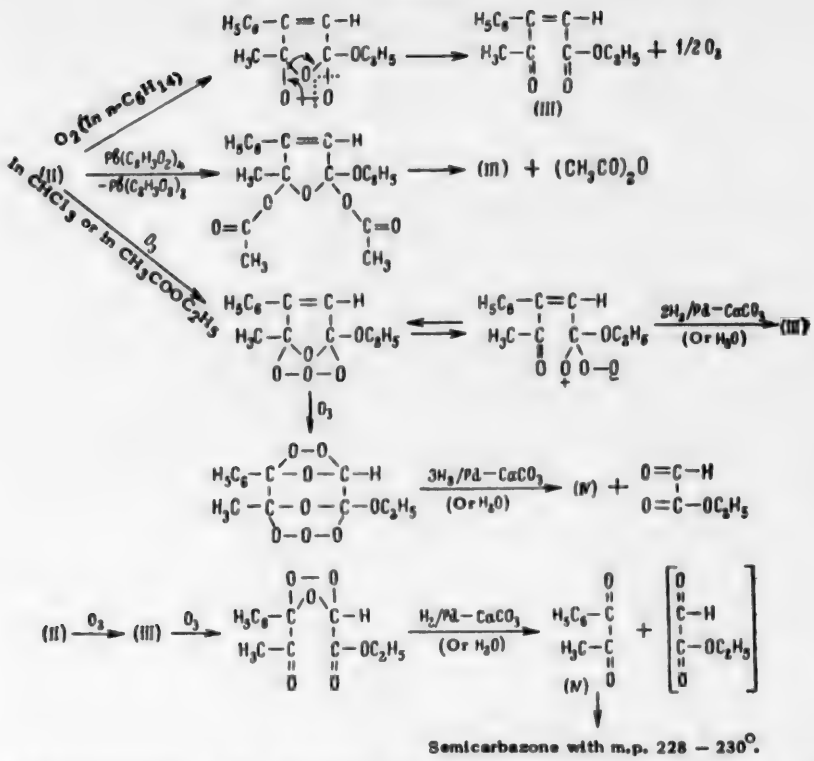
The question of the mechanism of the synthesis of furanes in the presence of copper sulfate is not sufficiently clear. It is possible that one of the reactants forms a complex compound with the catalyst which later reacts, leading to the production of a furane. In any case, the example given is the first unconditional indication of the fact that a free ethoxycarbonyl carbene is capable of reacting in the 1,3 position, possibly through a transformation (under the conditions of formation of the complex with the catalyst or under the influence of the catalyst) into the bipolar form (IIA). It is impossible, however, not to note that for acyl carbenes obtained by photochemical decomposition of the corresponding diazoketones, the possibility of reacting in the 1,3 position has been demonstrated in three cases [8-10]. However, in none of these cases did copper sulfate figure as a catalyst and an acetylenic hydrocarbon as a carbene acceptor.

The present work is devoted to a description of the reaction leading to the formation of (II) and its characteristics as a furane derivative. The experimantal conditions and the conditions for isolating (II) from the reaction mixture are given in the experimental part. The most rational means of isolating (I) and diethyl fumarate from the mixture is not fractional distillation but alkaline hydrolysis; under these conditions, (II) does not change. The yield is 48% calculated on the hydrocarbon which has reacted. The substance (II) is extremely unstable to oxidants. On storage in an open vessel, it is converted into the ester (III). The same result may be achieved by passing dry oxygen into a solution of (II) in n-hexane. The ester (III) may also be obtained by oxidizing (II) in anhydrous benzene with lead tetraacetate and by ozonization of (II) at -20° and -60°. By-products of the ozonization found were the diketone (IV) and benzoic acid. It is possible that (IV) is formed as a result of the addition of a second molecule of ozone to the ozonide (II); however, the possibility of obtaining (IV) as a result of the ozonization of (III) is not excluded.

The formation of the latter under the conditions of ozonization must be achieved if the oxidizing action of molecular oxygen on (II), which was mentioned above, is taken into consideration. The above-mentioned reactions of oxidation and ozonization of (II) are represented in schemes 1 and 2.

The fission of the furane ring under the action of oxygen [11], lead tetraacetate [12], and ozone [13] has been described for various furane derivatives, but not for 5-alkoxy derivatives. The latter have been very little studied in general [14]. From our results, it may be concluded that the presence of an ethoxyl group in position 5 of the furane ring increases its oxidizability. Although not one of the intermediate compounds shown in schemes 1 and 2 was isolated from the reaction medium (at least in the individual state, including the ozonides), the proposed mechanisms must be considered probable. The idea of them was borrowed from the work of other authors investigating the action of the same reagents on various furane derivatives [11-13].

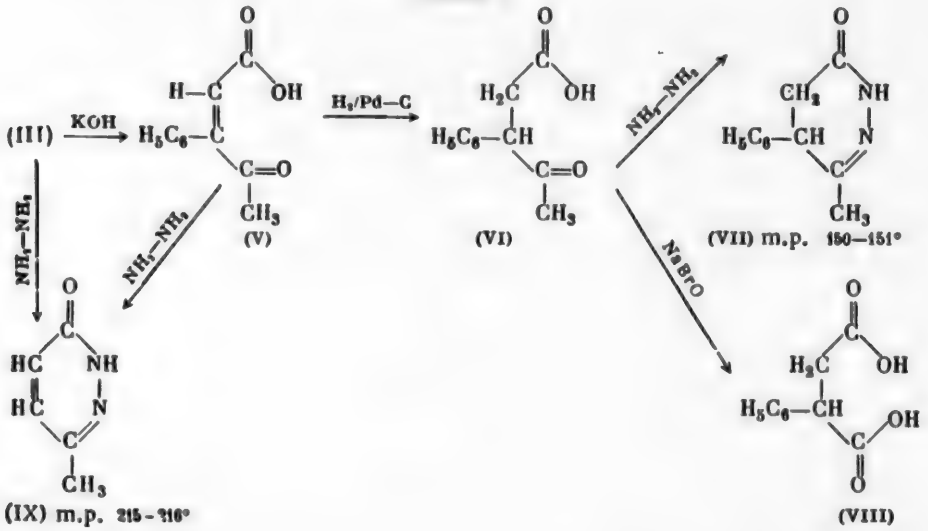
Scheme 1



The ester (III) is not described in the literature. Its IR spectrum contained bands at 5.96 (very strong) and 5.82 (very strong) μ, which are characteristic for the presence in the ester (III) of a ketonic carbonyl and an ester group, and bands at 6.06 (medium) and 6.25 (medium) μ, which must be associated with the presence in the ether (III) of an olefinic bond and an aromatic nucleus. Like an ester of an α,β-unsaturated γ-ketoacid, (III) gives with hydrazine hydrate a solid pyridazine (IX) used for the identification of (III) (scheme 2). The same compound (IX) is formed by the action of hydrazine hydrate on the acid (V) – the product of the alkaline hydrolysis of (III). This points to an identity in the structures of (III) and (V).

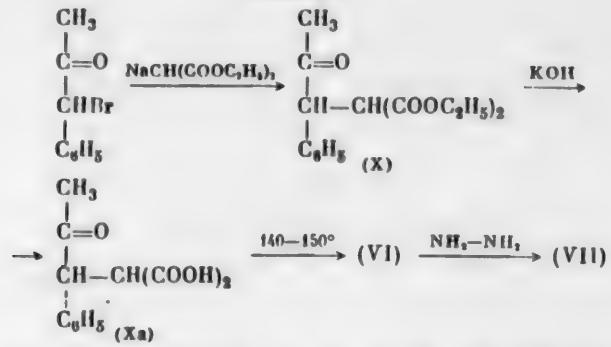
With the aim of establishing the structure of the acid (V), it was hydrogenated with hydrogen in the presence of Pd to the acid (VI), the structure of which in its turn was confirmed, in the first place, by oxidation with sodium hypobromite (scheme 2) and, in the second place, by an independent synthesis starting from methyl α-bromobenzyl ketone and sodiomalonic ester (scheme 3).

Scheme 2



The two preparations of the acid (VI) obtained by different routes gave one and the same solid dihydropyridazine (VII) (schemes 2 and 3).

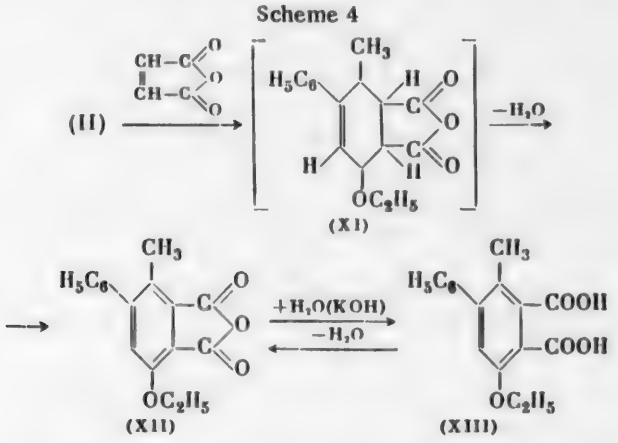
Scheme 3



Finally, further confirmation of the structure of (III) was obtained by its ozonization. Ozonization and subsequent decomposition of the ozonide by hydrogen (Pd / $CaCO_3$) led to the formation of the diketone (IV) (78.8%), characterized in the form of its semicarbazone (scheme 1), and a small amount of benzoic acid. The other product of the ozonolysis – the ester of glyoxylic acid–was not isolated.

Thus, the structure of (III) must be considred established. This, in its turn, gives the right to consider the oxidation and ozonization of (II) as confirming this structural formula. One of the extremely persuasive indications in favor of assigning (II) to the furane series is the ability of this compound to take part in the diene synthesis (scheme 4). We found this reaction of (II) as a result of the performance of supplementary experiments [6].

Scheme 4



The primary reaction product (XI) proved to be unstable, and under the reaction conditions was converted, with loss of water, into (XII). The formula of (XII) was confirmed by the data of elementary and functional analysis, and also by its conversion into the acid (XIII). The later, on heating, was reconverted into (XII).

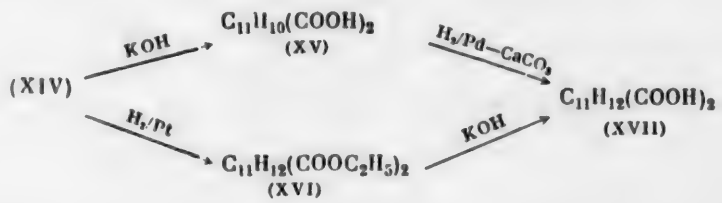
Not only the data of the chemical, but also those of the spectroscopic. investigation of the product of condensation of diazoacetic ester with 1-phenylpropyne are in agreement with formula (II). The strong absorption at 6.30 μ together with the medium absorption at 6.17 μ in the IR spectrum of this compound may be assigned [15] to the presence of the conjugated system of bonds of the furane ring of (II) [earlier [3], when formula (IA) was used instead of (II), the band at 6.30 μ was associated with an "anomalous" – due to the presence of a cyclopropene ring – absorption of the carbonyl group of the "ester"]. The absorption at 7.65 μ (very strong) apparently must be assigned to the stretching vibrations of the C–O bond of the ring, and that at 8.50 μ (strong) to the presence in (II) of an ethoxyl group [16]. The bands in the spectrum at 6.26 (medium) and 6.65 (strong) μ may be assigned to the phenyl group.

As already mentioned in the preliminary communication [1], the reaction between diazoacetic ester and 1-phenylpropyne in the presence of copper sulfate is accompanied by the formation (with a yield of 13.5%) of the ester

(XIV), corresponding in composition to the product of condensation of two molecules of diazo compound with one molecule of hydrocarbon.

$$H_3C_6-C\equiv C-CH_3 + 2N_2{:}CHCOOC_2H_5 \xrightarrow{CuSO_4} \underset{(XIV)}{C_{11}H_{10}(COOC_2H_5)_2} + 2N_2$$

The structure of (XIV) has not been established. It is known only that it hydrolyzes with alkali to the dibasic acid (XV), and on catalytic hydrogenation absorbs 1 mole of hydrogen with the formation of the ester (XVI).



It is possible that (XVI) is a product of a secondary reaction of (I) with the diazoacetic ester.

EXPERIMENTAL

1. Condensation of ethyl diazoacetate with 1-phenylpropyne in the presence of copper sulfate. 5-Ethoxy-2-methyl-3-phenylfurane (II). Sixty grams of well-purified [18] diazoacetic ester was added slowly (~ 8 g in 1 hour) in drops with mechanical stirring and in an atmosphere of nitrogen to a reaction mixture formed from 40 g of 1-phenylpropyne (with b.p. 74-75° at 15 mm, n_D^{20} 1.5638 [17]), 40 ml of cyclohexane, and 0.5 g of anhydrous copper sulfate, heated to 90°. After the evolution of nitrogen from the reaction mixture had commenced, the heat was reduced to 70° (temperature of the mixture). After completion of the reaction, the mixture was transferred in a current of nitrogen to a Schott filter and filtered from the residue of catalyst. The solvent (27.3 g) was distilled off in a vacuum of 150 mm (b.p. 40-45°) from the filtrate, which was also kept from contact with atmospheric oxygen. The residue was distilled under a higher vacuum (see table).

Frac. No.	Content of the fraction	Boiling point (pressure in mm)	n_D^{20}	Wt. (g)	Found (%)		Calculated (%)	
					C	H	C	H
1	1-Phenylpropyne + diethyl fumarate	60—110° (10)	1.5410	20.5	—	—	—	—
2	(II) contaminated with (I)	90—95 (0.3)	1.5680	29.5	77.08, 77.19	6.62, 7.04	77.20 *	6.97
3	Intermediate (I, II, and XIV)	96—123 (0.3)	1.5310	4.2	—	—	—	—
4	(XIV)	124 -126 (0.3)	1.5142	10.3	70.73, 70.66	7.12, 7.13	70.83 **	6.94

* Calculated for $C_{13}H_{14}O_2$ (I or II).

** Calculated for $C_{17}H_{22}O_4$ (XIV).

In order to determine the composition of the first fraction and to recover the initial 1-phenylpropyne, the material of this fraction, amounting to 20.5 g, was heated for 2 hr on the water bath with 50 ml of 5% alcoholic caustic soda. On cooling the solution, 8.7 g (21% calculated on the weight of diazoacetic ester taken for the reaction) of disodium fumarate, which is sparingly soluble in alcohol, separated as a precipitate. For characterization, the salt was converted into the diphenacyl ester of fumaric acid [19], m.p. 197°. It was identified with a known sample. The alcoholic mother liquors remaining after the removal of the fumarate were diluted with water and the hydrocarbon separating in the form of a layer was distilled with steam. By means of an additional distillation of the hydrocarbon in vacuum, 10.6 g (26.5% of that used in the reaction) of 1-phenylpropyne, with b.p. 73-75° (15 mm), n_D^{20} 1.5630 [17], was obtained. Thus, the first fraction actually consists of a mixture of 1-phenylpropyne and diethyl fumarate.

The 2nd fraction could be a mixture of (I) and (II), judging from the value of n_D^{20} found for it [for pure (I) n_D^{20} is 1.5361* and for pure (II) n_D^{20} is 1.5773* *], and the result of elementary analysis (see table) agrees with (I) and (II) to an equal extent. The IR spectrum also indicated the presence of the ester (I) in the second fraction: the strong absorption at 5.78 μ is characteristic for the carbonyl group of an ester. The absorption of the C=O group of pure (I*) is in the same region.

Our task was to isolate pure (II). For this purpose, 29.5 g of the material of the second fraction was heated for 2 hours with 100 ml of a 5% solution of sodium methoxide in methyl alcohol. In order to exclude the oxidation of (II), the heating was carried out in an atmosphere of nitrogen. After the completion of the experiment, the solution was diluted with a large amount of water and the (II) was extracted with ether. The ethereal extracts were dried with $CaCl_2$, the ether was evaporated in a current of nitrogen, and the residue, consisting of almost pure (II), was distilled in vacuum. In this way, 24.2 g (48% calculated on the hydrocarbon which had reacted and 21.7% calculated on the diazoacetic ester) of analytically pure (II) was obtained.

B.p. 94-95° at 0.3 mm, d_4^{20} 1.0800, n_C^{20} 1.56919, n_D^{20} 1.57732, n_F^{20} 1.60029, MR_C 61.37, MR_D 62.08, MR_F 64.08. $C_{13}H_{14}O_2F_5$. Calculated: MR_C 58.36, MR_D 58.78, MR_F 60.55. $E\Sigma_C$ 1.48, $E\Sigma_D$ 1.63, $E\Sigma_F$ 1.74.

Found %: C 77.20, 77.18; H 7.10, 7.12; OC_2H_5 22.42, 2240. M 199.5, 199.9. $C_{11}H_9OOC_2H_5$. Calculated %: C 77.20; H 6.97; OC_2H_5 22.27. M 202.2.

Infrared spectrum (in μ): 6.17 (medium), 6.25 (medium), 6.30 (very strong), 6.37 (strong), 6.65 (medium), 6.89 (medium), 7.21 (strong), 7.65 (very strong), 8.35 (strong), 8.50 (very strong), 9.04 (medium), 9.51 (very strong), 9.84 (strong), 11.02 (strong).

UV spectrum: [1 % solution of (II) in n-C_6H_{14}] γ_{max} 295 mμ, Σ_{max} 26500.

The compound (II) consists of a colorless liquid which acquires a yellow color and readily changes on storage in the air.

The aqueous alcoholic mother liquors remaining after the removal of the (II) from the solution (see above) were concentrated to a volume of 50 ml and acidified with 10% sulfuric acid with the aim of isolating the acid corresponding to the ester (I). Under these conditions, 2.9 g of a very viscous oil was obtained, from which by repeated crystallization from a mixture of petroleum ether and acetone an acid with m.p. 137-139° was isolated in a yield of 0.4 g [a similar investigation of the ester (I) and the corresponding acid was described in the last communication of this series].

The 4th fraction consisted of the analytically pure ester (XIV). The yield was 10.3 g, or 13.5% calculated on the hydrocarbon which had reacted and 13.2% calculated on the initial diazoacetic ester.

B.p. 123-126 at 0.3 mm, d_4^{20} 1.0964, n_D^{20} 1.5142.

Found %: C 70.73, 70.66; H 7.17, 7.12; OC_2H_5 31.20, 31.30. Hydrolysis equivalent 143.0, 148.3, M 288.0, 286.9. $C_{11}H_{10}(COOC_2H_5)_2$. Calculated %: C 70.83; H6.94; OC_2H_5 31.25. Hydrolysis equivalent 144.1. M 288.3.

IR spectrum (in μ): 5.80 (very strong), 6.10 (weak)6.25 (medium), 6.65 (medium), 6.89 (medium), 7.22 (strong), 8.36 (very strong), 8.54 (very strong), 9.73 (strong), 10.95 (weak).

The ester (XIV) consisted of a colorless viscous oil differing from (II) in not being oxidized by atmospheric oxygen.

II. Determination of the structure of 5-ethoxy-2-methyl-3-phenylfurane (II). 1) Reaction with maleic anhydride: 6-ethoxy-3-methyl-4-phenylphthalic anhydride (XII). One gram of (II) was mixed with 1 gram of finely ground malic anhydride. During mixing, the evolution of heat and the appearance of a red color were observed. The mixture was heated for a further 20 minutes on the water bath. As a result, the color disappeared and the reaction product crystallized. To eliminate the excess of maleic anhydride, the crude (XII) formed was heated on the water bath with 20 ml of 50% aqueous ethanol. The compound (XII), sparingly soluble in alcohol, was filtered off and recrystallized from dioxane. M. p. 276-278° Colorless needles, insoluble in ether, acetone, chloroform, and methyl alcohol; soluble in dioxane and toluene. Yield 1.0 g (71.4%).

Found %: C 72.04, 72.16; H 5.02, 4.98; OC_2H_5 15.80, 15.68. $C_{15}H_9O_3OC_2H_5$. Calcu. %: C72.34; H 4.96; OC_2H_5 15.92.

2) Hydrolysis of (XII): 6-Ethoxy-3-methyl-4-phenylphthalic acid (XIII). A mixture of 1 g of (XII) and 25

* We obtained pure (I) in collaboration with S. P. Korshunov. A future communication will be devoted to a description of this work.

* * See below.

ml of a 3% methanolic solution of caustic potash was heated on the water bath for 0.5 hr. After the usual working up and acidification of the solution with dilute sulfuric acid, the substance (XIII) was obtained in the form of a viscous oil which rapidly crystallized. For purification, the product was crystallized from a mixture of petroleum ether and acetone (4 : 1). M.p. 124° (decomp.). Colorless prisms, readily soluble in acetone and ether, sparingly soluble in petroleum ether and ethyl alcohol. The yield of (XIII) was 0.8 g (75%).

Found %: C 65.63; H5.36; OC_2H_5 14.32. Equiv. 151.8. $C_{13}H_9(OC_2H_5)(COOH)_2$. Calculated %: C 65.81; H5.19; OC_2H_5 14.52. Equiv. 150.1.

On heating, (XIII) split out water and was reconverted into the initial anhydride (XII).

3) Oxidation of (II) with oxygen. Ethyl ester of 4-oxo-3-phenylpent-2-en-1-oic acid (III). On storing (II) in the air at room temperature, n_D changed rapidly. After 24 hours it approximated to the refractive index of the final oxidation product of (II) – the ester (III), which may also be obtained by the action of lead tetraacetate and ozone on (II) (see below). An analytically pure preparation of (III) has n_D^{20} 1.5305.

It is most convenient to carry out the oxidation of (II) with molecular oxygen in an organic solvent in the following way. A slow current of dry oxygen (~ 1 l. per hour) at 15-20° was passed through a solution of 5 g of the substance (II) in 30 ml of n-hexane. On reacting with oxygen, the transparent solution became turbid and (III) deposited on the bottom of the reaction vessel as a heavy oil. The total amount of oxygen passed was 10.5 l. (16°, 759 mm). After removing the solvent, the oil (III) weighed 5.5 g. The yield was quantitative; n_D^{20} 1.5305, d_4^{20} 1.1058. After distillation in vacuum it formed a yellow liquid. It gives no color reaction with an alcoholic solution of ferric chloride, and gives no precipitate with an acetic acid solution of semicarbazide or on heating with phenylhydrazine. On the other hand, the corresponding solid derivative is readily formed on heating (III) with an alcoholic solution of hydrazine hydrate. The data given below relate to the ester (III).

B.p. 117-118° at 0.3 mm, d_4^{20} 1.1058, n_D^{20} 1.5305.
Found %: C 71.45, 71.32; H 6.52, 6.58; OC_2H_5 20.52, 20.48. M 212.6, 216.0. $C_{13}H_{14}O_3$. Calculated %: C 71.54; H 6.46; OC_2H_5 20.64. M 218.2
IR spectrum: 5.82 (very strong), 5.96 (very strong), 6.06 (medium), 6.25 (medium) μ.

4) Ozonization of (II). a) Experiment 1. A current of 4% ozone was passed into a solution of 5 g of (II) in 30 ml of $CHCl_3$ at -20° until 1.2378 g of O_3 or 104% of the theoretical amount calculated on the basis of 1 mole of ozone per 1 mole of (II) had been consumed. The chloroform was removed in vacuum. The residue consisted of a viscous oil of the ozonide with n_D^{20} 1.5030. Weight 6.0 g. The ozonide was decomposed with water (50 ml) on the boiling water bath (4 hours). The decomposition products of the ozonide were extracted with ether. The ethereal extract was found to contain the ester (III) contaminated with the diketone (IV) (see below) and benzoic acid, and the aqueous layer was found to contain formic acid, which is not readily extracted by ether from aqueous solution. To separate the benzoic acid from the (III), the ethereal extract was washed with a solution of sodium bicarbonate. After acidification of the soda solution, 0.5 g of benzoic acid with m.p. 121-122° was obtained.

The crude (III) obtained from the ethereal extract weighed 3.1 g (60%), n_D^{20} 1.5290 [for the pure ester (III), n_D^{20} 1.5305]. The action of hydrazine hydrate in alcoholic solution yielded the pyridazine (IX) with m.p. 215-216°. As in the case of the pure product, no solid derivative was obtained with an acetic acid solution of semicarbazide, but the first portions of the distillate obtained on vacuum distillation of the crude (III) gave a small precipitate (0.15 g) of a semicarbazone with m.p. 228-230° [20] with this reagent. This result indicates the presence of the diketone (IV) in the (III) obtained.

The formic acid in the aqueous solution was determined by the quantitative calomel method. The amount of HCOOH found was 0.076 g, which corresponds to 6.7% of that calculated according to formula (II). The dimedone test for the presence of formaldehyde in the solution was negative.

b) Experiment 2. A current of 4% ozone was passed into a solution of 3.0 g of (II) in 30 ml of $CH_3COOC_2H_5$, the solution being cooled externally to -60°. The ozonization was completed when 0.825 g of O_3 had been absorbed, which corresponds to 116% of that calculated on the basis of 1 mole of O_3 per 1 mole of (II). Then the solution of the ozonide was transferred into a catalytic hydrogenation apparatus and was saturated with hydrogen in the presence of 1 g of 2.5% Pd/$CaCO_3$ with mechanical stirring. Only 158 ml of H_2 (0°, 760 mm) was absorbed, which corresponds to 47.5% of the calculated amount. After the completion of the hydrogenation, the catalyst was filtered off and the ethyl acetate was removed in vacuum. The residual oil was dissolved in ether and washed with a 10% solution of sodium bicarbonate. After acidification of the soda extracts, 0.35 g of benzoic acid with m.p. 121-122°

was obtained. The ethereal solution yielded 2.2 g (68%) of the crude ester (III), which, as in experiment 1, contained the diketone (IV) as an impurity. The latter was detected by means of a semicarbazide test.

5. Oxidation with lead tetraacetate. Two grams of (II) was dissolved in 25 ml of benzene distilled over sodium. The solution was heated to 60° and 4.5 g of lead tetraacetate was added to it with vigorous stirring. The reaction mixture was heated for 20 minutes at 80° and cooled to room temperature, and the lead acetate which separated was filtered off. The benzene was distilled off from the filtrate in a low vacuum in a current of air. The reaction product obtained as residue consisted of a heavy colorless oil. A qualitative test with sodium selenite indicated the presence of acetic anhydride in this oil [21]. No acetic acid was found. The acetic anhydride was removed from the reaction product by heating it in a vacuum of 10 mm. The residue was distilled in vacuum.

B.p. 117-118° at 0.3 mm, n_D^{20} 1.5305, d_4^{20} 1.1058.
Found %: C71.42, 71.28; H 6.67, 6.65; OC_2H_5 20.52, M 217.7, 220.8. $C_{13}H_{14}O_3$. Calculated %: C 71.50; H 6.63; OC_2H_5 20.64. M 218.

Judging from the analytical data and the constants, the compound analyzed is the ester (III). Yield 1.5 g (70%). For definitive identification with (III), the compound obtained was converted into the solid pyridazinone (IX) with m.p. 215-216°, using hydrazine hydrate.

III. Determination of the structure of the ester (III). 1) Reaction of (III) with hydrazine hydrate. 3-Methyl-4-phenylpyridazin-6-one (IX). One gram of hydrazine hydrate was added to a solution of 1 g of (III) in 5 ml of alcohol. Heat was developed on mixing. The mixture was heated for a further 20 minutes on a sand bath. On cooling, colorless crystals of (IX) separated from the solution; after filtration and a single crystallization from 50% alcohol they melted at 215- 216°. Yield 0.7 g (82.3%).

Found %: C 70.81, 70.69; H 5.57, 5.49; N 15.35, 15.65. M 180.0, 182.6. $C_{11}H_{10}O_2$. Calculated %: C 70.95; H 5.41; N 15.44. M 186.2.
IR spectrum (in 0.04 M alcohol): λ_{max} 300 mμ, ε_{max} 3750; λ_{max} 240 mμ, ε_{max} 20,000.

The substance (IX) has not been described in the literature. It is also formed by the action of hydrazine hydrate on the acid (V) (see below).

2) Hydrolysis of (III). 4-Oxo-3-phenylpent-2-enoic acid (V). (β-Acetylcinnamic acid). A mixture of 2.2 g of (III) and 35 ml of 2% caustic potash in methanol was heated for 1 hour on the boiling water bath. After cooling, the solution was brought to neutrality (to phenolphthalein) by the addition of dilute sulfuric acid, and the ethyl alcohol was distilled off with steam. The remaining aqueous solution was acidified with 10% sulfuric acid, with external ice cooling, and the acid (V) which separated was extracted with ether. After evaporating off the ether and distilling the residue in vacuum, 1.5 g (77.8%) of the acid (VI) was obtained in the form of a viscous yellow oil with b.p. 148-151° at 0.3 mm.

Found %: C 69.58, 69.27; H 5.45, 5.32. Equiv. 192.3, 189.4. $(C_{10}H_9O)COOH$. Calculated %: C 69.46; H 5.24. Equiv. 190.2.

3) Hydrogenation of the acid (V). 4-Oxo-3-phenylpentanoic acid (VI). A solution of 1.0 g of (V) in 15 ml of 95% alcohol and 0.2 g of Pd, deposited on carbon, were placed in a catalytic hydrogenation apparatus and saturated with hydrogen with mechanical shaking. The consumption of hydrogen was 116 ml (0°,760 mm). Calculated for the hydrogenation of the one double bond in (V): 120 ml H_2. After filtering the solution from the catalyst and evaporating the alcohol in vacuum, 0.89 g of the acid (VI) was obtained in the form of a viscous yellow oil.

Found equiv.: 195.0, 193.2. $(C_{10}H_{11}O)COOH$. Calculated equiv.: 192.2.

The acid gave a silver salt (decomposing in the light), which was analyzed.

Found %: C 44.32; H 3.91; Ag 35.90. $C_{11}H_{11}O_3Ag$. Calculated %: C 44.17; H 3.70; Ag 36.07.

4) 3-Methyl-4-phenyl-4,5-dihydropyridazin-6-one (VII). A mixture of 0.25 g of the acid (VI) obtained by the hydrogenation of (V), 0.5 g of hydrazine hydrate, and 2.5 ml of 95% alcohol was boiled for 20 minutes on a sand bath. After cooling, crystals of (VII) separated. After crystallization from alcohol, it had m.p. 150-151°. Yield 0.15 g (60%).

Found %: N 14.76. $C_{11}H_{12}ON_2$. Calculated %: N 14.87.

5) Oxidation of (VII) with sodium hypobromite. A solution of sodium hypobromite prepared from 3 g of bromine and 50 ml of 10% caustic soda was added to a solution of 1 g of the acid in 10 ml of 10% caustic soda cooled to 0°. The carbon tetrabromide [m.p. 90-94°, 0.9 g (53%)] which separated as a precipitate was filtered off, and the filtrate was acidified with 10% sulfuric acid and extracted with ether. The crude phenylsuccinic acid (VIII) obtained from the ethereal solution was pressed out on a porous plate and recrystallized from water. M.p. 164-166° (literature data: m.p. 167° [16]). Yield of (VIII) 0.6 g (60%).

6) Independent synthesis of (VI). To a solution of sodiomalonic ester in anhydrous alcohol prepared from 3.0 g of sodium, 21 g of diethyl malonate, and 100 ml of anhydrous alcohol, 26 g of phenylacetylbromomethane [22] was added in drops with mechanical stirring. After this, the reaction mixture was boiled and stirred for 3 hours.

The solution obtained was cooled to room temperature and poured into water. The organic layer which was produced was separated from the aqueous layer and the latter was extracted several times with ether. The ethereal extracts were united with the organic layer, the solution was dried with calcium chloride, and the ether was distilled off in vacuum. The residual liquid (25 g) consisted of the impure diethyl ester (X). The ester (X) was heated on the water bath with 125 ml of 10% methanolic KOH. After the completion of the hydrolysis, the solution was diluted with water, the excess of alkali was neutralized with acid and the methyl alcohol was distilled off with steam. The solution remaining in the distillation flask was cooled to 0° and carefully acidified with 10% sulfuric acid. The dibasic acid which separated under these conditions had the form of a viscous dark-colored oil. It was separated from the aqueous layer using ether and, after distillation of the solvent, was subjected to decarboxylation. For this, it was heated in a vacuum of 1 mm at 140-150° until the evolution of carbon dioxide ceased. The residual crude acid (VI) was distilled in vacuum. B.p. 153-157° at 0.3 mm. Yield 6.3 g, or 27% calculated on the initial phenylacetylbromomethane.

Found %: C 68.41, 68.32; H 6.29, 6.18. Equiv. 189.8. $(C_{10}H_{11}O)COOH$. Calculated %: C 68.73; H 6.29. Equiv. 192.2.

From 1 g of the acid (VI) and 1 g of hydrazine hydrate in 10 ml of alcohol, 0.4 g (44%) of the dihydropyridazinone (VII) with m.p. 149-151° (from 50% alcohol) was obtained. A mixed melting point test with the preparation of (VII) described above showed no depression of the melting point. This indicates that the acid (VI) obtained by the hydrogenation of (V) is identical with the acid (VI) obtained by independent synthesis from phenylacetylbromomethane.

7) Ozonization of the ester (III). A mixture of 3 g of (III) and 30 ml of purified ethyl acetate was placed in an ozonization vessel which was cooled externally with a mixture of ice and common salt while a slow current (8-10 l. per hr) of 4% ozone was passed through it. After 0.79 g of O_3, calculated as pure ozone, had been absorbed [calculated for the double bond of (III): 0.66 g of O_3], the ozonization was discontinued and the solution of ozonide was transferred to a catalytic hydrogenation vessel with 1 g of $Pd/CaCO_3$ catalyst. The ozonide was decomposed with hydrogen, the apparatus being shaken mechanically: 212 ml of H_2 (18°, 767 mm) were consumed. After filtration from the catalyst, the solvent was evaporated in vacuum without heating. The residue contained the oily diketone (IV) contaminated with crystals of benzoic acid. To isolate the benzoic acid, the reaction product was dissolved in ether and the ethereal solution was extracted with 10% sodium bicarbonate. The combined soda extracts after acidification yielded 0.3 g (15%) of benzoic acid with m.p. 119-120°. It was identified by the mixed melting point test. The ethereal solution yielded 1.8 g (78.8%) of the diketone (IV), n_D^{20} 1.5300. The latter was characterized in the form of the disemicarbazone, which is described in the literature [20]. Colorless crystals, insoluble in the usual organic solvents, with m.p. 228-230°.

Found %: N 32.14, 31.90. $C_{11}H_{14}O_2N_6$. Calculated %: N 32.04.

IV. Investigation of the ester (XVI) with the composition $C_{11}H_{10}(COOC_2H_5)_2$. This ester was obtained as a by-product of the condensation of diazoacetic ester with 1-phenylpropyne in the presence of $CuSO_4$. In contrast to the ester (II) it is stable to the action of atmospheric oxygen. A cold solution of potassium permanganate oxidizes the ester (XIV) with difficulty. On heating it with permanganate, benzoic acid is formed. No other oxidation products were isolated. On ozonolysis and subsequent decomposition of the ozonide with water, benzoic acid was again isolated, together with a small amount of a liquid substance giving a dark red coloration with an alcoholic solution of ferric chloride. This substance was not investigated.

Hydrolysis of (XIV). Acid (XV) of the composition $C_{11}H_{10}(COOH)_2$. A mixture of 2 g of the ester (XIV) and 40 ml of a 5% solution of caustic potash in alcohol was boiled on the water bath for 1.5 hours. After cooling, the

solution was neutralized with dilute sulfuric acid (to phenolphthalein) and the alcohol was distilled off with steam. The residue in the distillation flask was concentrated to a volume of 25 ml and acidified with a calculated amount of 10% sulfuric acid. The crude acid (XV) which separated weighed 1.5 g. After two crystallizations from 70% alcohol it had m.p. 191-192.5. Yield of (XV), 1.2 g (75%).

Found %: C 67.23, 67.39; H 5.43, 5.45. Equiv. 117.7, 117.3. $C_{11}H_{10}(COOH)_2$. Calculated %: C 67.24; H 5.20. Equiv. 116.1.

The acid (XV) is readily soluble in alcohol, ether, and acetone, sparingly soluble in benzene and water. The aqueous solution of the Na or K salt of the acid rapidly decolorizes a solution of permanganate, but only benzoic acid can be isolated as a result of the oxidation. It reacts slowly with a solution of ozone in chloroform. Benzoic acid and a small amount of unchanged initial acid were found in the ozonization products.

Hydrogenation of the ester (XIV). The ester (XVI) of composition $C_{11}H_{12}(COOC_2H_5)_2$. A mixture of 3.6 g of the ester (XIV), 30 ml of alcohol (95%), and 0.4 g of Pt black was placed in a catalytic hydrogenation apparatus. Hydrogenation was carried out with mechanical stirring and heating to 45°. Hydrogen was absorbed very slowly at room temperature. The total amount of hydrogen consumed was 293.6 ml (0°, 760 mm), or 110% of that calculated for one double bond in (XIV). The hydrogenation product – the ester (XVI) – was distilled in vacuum. (XVI) is a colorless viscous oil with b.p. 143-145° at 0.3 mm. Yield 2.9 g (86.1%).

d_4^{20} 1.0848, n_D^{20} 1.5070.

Found %: C 70.28, 70.21; H 7.68, 7.71; OC_2H_5 31.12, 30.96. $C_{11}H_{12}(COOC_2H_5)_2$. Calculated %: C 70.32; H 7.63; OC_2H_5 31.03.

Hydrolysis of (XVI). The acid (XVII) of composition $C_{11}H_{12}(COOH)_2$. A mixture of 1 g of the ester (XVI) and 25 ml of 5% alcoholic NaOH was heated for 2 hours on the water bath. The salt of the acid (XVII) separating as a precipitate at the end of the hydrolysis was brought into solution by dilution with water, the alcohol was distilled off with steam, and the residual aqueous solution was acidified with 10% sulfuric acid. The crude acid obtained was recrystallized from a mixture of benzene and acetone, m.p. 184-185°. Yield 0.6 g (75%).

Found: equiv. 118.10, 117.21. $C_{11}H_{12}(COOH)_2$. Calculated : equiv. 117.12.

SUMMARY

It has been shown that the reaction of ethyl diazoacetate (1 mole) with the acetylenic hydrocarbon 1-phenylpropyne (0.67 mole) in the presence of anhydrous copper sulfate (0.003 mole) as catalyst, with cyclohexane as solvent, yields 5-ethoxy-2-methyl-3-phenylfurane (II) and the ester of a dicarboxylic acid with one double bond of the composition $C_{11}H_{12}(COOC_2H_5)_2$, with yields of 48 and 13.5% respectively, calculated on the hydrocarbon which has reacted. In addition, the same reaction yields, as an impurity in the (II), a small amount of the ethyl ester of 1-methyl-2-phenyl-$\Delta^{1,2}$-cyclopropene-3-carboxylic acid. The properties and various reactions of 5-ethoxy-2-methyl-3-phenylfurane have been studied with a view to confirming its structure. The given reaction is the first example of the reaction of a biradical of an ethoxycarbonyl carbene formed by the catalytic decomposition of diazoacetic ester in the 1,3 position.

LITERATURE CITED

1. I. A. D'yakonov, M. I. Komendantov, Vestn. LGU 22, ser. fiz. khim., No. 4, 166 (1956).
2. I. A. D'yakonov, M. I. Komendantov, ZhOKh 29, 1749 (1959).
3. I. A. D'yakonov, M. I. Komendantov, I. Gokhmanova, R. Kostikov, ZhOKh 29, 3850 (1959).
4. R. Breslow, J. Am. Chem. Soc. 79, 5318 (1957).
5. R. Breslow, R. Winter, M. Battiste, J. Org. Ch. 24, 414 (1959).
6. I. A. D'yakonov, M. I. Komendantov, ZhOKh 31, 3483 (1961).
7. R. Breslow, D. Chipman, Chem. Ind. 1960, 1105.
8. K. B. Wiberg, T. W. Hutton, J. Am. Chem. Soc. 76, 5367 (1954).
9. A. S. Kende, Ph. D. Thesis Harvard, 1956; cited in: P. Yotes, E. W. Robb, J. Am. Chem. Soc. 79 5761 (1957).
10. F. Weygand, Ang. Chem. 73, 70 (1961).
11. J. Schenk, Ber. 80, 289 (1947).
12. Chi-Kand Dien, R. L. Lutz, J. Org. Ch. 22, 1355 (1957).
13. Ph. Bailey, H. Colomb, J. Am. Chem. Soc. 79, 4238 (1957).

14. D. G. Manly, E. D. Amstutz, J. Org. Ch. 21 516 (1956).
15. L. Bellamy, Infrared Spectra of Molecules [Russian translation] IL, 47, 136 (1957).
16. Sint. org. prep. 1, 442 (1949).
17. E. Bergmann, A. Bondi, Ber. 66, 278 (1933).
18. L. Gatterman, H. Wieland, Die Praxis des organischen Chemikers [Russian translation] M.-L., GKhI, 317 (1948).
19. W. S. Johnson, R. J. Shannon, R. A. Reid, Organic Reagents for Organic Analysis [Russian translation] IL (1948).
20. K. V. Auwers, Ber. 50,1612 (1917).
21. K. Bayer, Analysis of Organic Compounds [Russian translation] IL, 286 (1953).
22. T. I. Temnikova, ZhOKh 8, 1025 (1938).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

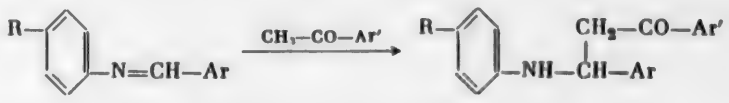
CATALYTIC SYNTHESIS OF β-ARYLAMINO KETONES

N. S. Kozlov and A. D. Nikolaev

The D.N. Pryanishnikov Perm Agricultural Institute
Translated from Zhurnal Obshchei Khimii, Vol 31, No. 12,
pp. 3894-3896, December, 1961
Original article submitted July 11, 1960

The condensation of Schiff's bases with aliphatic – aromatic ketones has been studied earlier. Thus, Francis [1] studied the reaction of benzylideneaniline, benzylidene-p-toluidene, and benzylidene-p-nitroaniline with dibenzyl ketone and deoxybenzoin. He subsequently [2] studied the reaction of benzylideneaniline with methyl, ethyl, and propyl benzyl ketones. Then Mayer [3] studied the condensation of benzylideneaniline, benzylidene-p-toluidene, and benzylidene-2-naphthylamine with acetophenone and of benzylideneaniline with p-methylacetophenone, and subsequently the reaction of benzylideneaniline with ethyl phenyl ketone [4]. In all these investigations, the reaction was carried out in the presence of alkali, and the corresponding β-arylamino ketones were obtained as the main products. Recently, this reaction has been studied by one of us [5], but in the presence of an acid catalyst. Various Schiff's bases and various aliphatic – aromatic ketones were used. The present work is a continuation of these investigations.

Starting from various Schiff's bases and acetophenone and p-methoxyacetophenone, a series of β-arylamino ketones was synthesized, the constants and analysis of which are given in the table. We consider the synthesis of β-arylamino ketones to be the result of the addition of a molecule of the aliphatic – aromatic ketones to the azomethine bond of the Schiff's base, which may be represented by the following scheme:



The chemical nature of the compounds synthesized was shown by their ability to undergo the hydramine decomposition under conditions similar to those described in previous communications.

EXPERIMENTAL

The synthesis of p-tolylaldehyde was carried out by the method of reference [6]. A reaction mixture consisting of 0.01 mole of the Schiff's base, 0.01 mole of the aliphatic – aromatic ketone, 10-15 ml of alcohol, and 1 g of the hydrochloride of the amine from which the Schiff's base was derived was heated on the water bath for 20-30 minutes. After cooling, the precipitate which separated was filtered off, treated with aqueous ammonia, and crystallized from a mixture of alcohol and benzene. The hydramine decomposition of the β-arylamino ketones synthesized was carried out by a method which has already been described in the literature [5]. On hydramine decomposition, the compounds (I-IX) yielded 4-methylchalcone with m.p. 96-97°, and compounds (X-XVII) yielded 4-methyl-4'-methoxychalcone with m.p. 126-127°. Then, starting from p-tolylaldehyde and acetophenone and methoxyacetophenone, the chalcones obtained above were synthesized. Mixed melting point tests of the chalcones synthesized in this way and obtained by hydramine decomposition showed no depression of the melting points.

SUMMARY

The condensation of Schiff's bases obtained from aromatic amines and p-tolylaldehyde with acetophenone and methoxyacetophenone has been studied. Seventeen β-arylamino ketones not described in the literature have been synthesized.

β-Arylamino Ketones of the General Formula $R-NH-\underset{\displaystyle C_6H_4CH_3}{CH}-CH_2COR_1$

$R_1 = C_6H_5$ (I—IX); $C_6H_4OCH_3$ (X—XVII)

Compound No.	R	Name of compound	Empirical formula	Melting point	% N		Yield (in %)
					found	calcu.	
(I)	C_6H_5	Phenyl β-anilino-β-p -tolylethyl ketone	$C_{22}H_{21}ON$	134-136°	3.11, 3.06	3.17	28
(II)	p-$CH_3C_6H_4$	Phenyl β-p -toluidino-β- tolylethyl ketone	$C_{23}H_{23}ON$	149-151	4.24, 4.13	4.25	36
(III)	m-$CH_3C_6H_4$	Phenyl β-m -toluidino-β-p tolylethyl ketone	$C_{23}H_{23}ON$	113-114	4.16, 4.05	4.25	35
(IV)	p-ClC_6H_4	Phenyl β-p -chloroanilino-β-p -tolylethyl ketone	$C_{22}H_{20}ONCl$	155-156	4.04, 4.11	4.01	48
(V)	p-BrC_6H_4	Phenyl β-p -bromoanilino-β-p -tolylethyl ketone	$C_{22}H_{20}ONBr$	170-171	3.40, 3.41	3.55	53
(VI)	p-IC_6H_4	Phenyl β-p -iodoanilino-β-p -tolylethyl ketone	$C_{22}H_{20}ONI$	165	3.11, 3.06	3.17	28
(VII)	p-$CH_3OC_6H_4$	Phenyl β-p -anisidino-β-p -tolylethyl ketone	$C_{23}H_{23}O_2N$	135-136	3.87, 3.86	4.05	29
(VIII)	p-$NO_2C_6H_4$	Phenyl β-p -nitroanilino-β-p -tolylethyl ketone	$C_{22}H_{20}O_3N_2$	165-166	7.50, 7.48	7.77	35
(IX)	m-$NO_2C_6H_4$	Phenyl β-m -nitroanilino-β-p -tolylethyl ketone	$C_{22}H_{20}O_3N_2$	117-119	7.65, 7.75	7.77	38
(X)	p-$CH_3C_6H_4$	p -Methoxyphenyl β-p -toluidino-β-p -tolylethyl ketone	$C_{24}H_{25}O_2N$	142-144	3.65, 3.66	3.89	29
(XI)	m-$CH_3C_6H_4$	p -Methoxyphenyl β-m -toluidino-β-p -tolylethyl ketone	$C_{24}H_{25}O_2N$	125-127	3.75, 3.70	3.89	40
(XII)	p-ClC_6H_4	p -Methoxyphenyl β-p -chloroanilino-β-p -tolyethyl ketone	$C_{23}H_{22}O_2NCl$	149-151	3.62, 3.57	3.69	42
(XIII)	p-BrC_6H_4	p -Methoxyphenyl β-p -bromoanilino-β-p -tolylethyl ketone	$C_{23}H_{22}O_2NBr$	156-157	3.24, 3.28	3.30	51
(XIV)	p-IC_6H_4	p -Methoxyphenyl β-p -iodoanilino-β-p -tolylethyl ketone	$C_{23}H_{22}O_2NI$	155-156	2.90, 2.91	2.97	54
(XV)	p-$CH_3OC_6H_4$	p -Methoxyphenyl β-p -anisidino-β-p -tolylethyl ketone	$C_{24}H_{25}O_3N$	142-143	3.58, 3.65	3.73	30
(XVI)	p-$NO_2C_6H_4$	p -Methoxyphenyl β-p -nitroanilino-β-p -tolylethyl ketone	$C_{23}H_{22}O_4N_2$	134-135	7.13, 7.09	7.17	33
(XVII)	m-$NO_2C_6H_4$	p -Methoxyphenyl β-m -nitroanilino-β-p -tolylethyl ketone	$C_{23}H_{22}O_4N_2$	123-134	7.24 7.31	7.17	35

LITERATURE CITED

1. E. Francis, J. Chem. Soc. 75,865 (1899); 77, 1191 (1900); 79, 441 (1902; 81, 441 (1904).
2. E. Francis, J. Chem. Soc. 81, 956 (1904).
3. Ch. Mayer, Bull. Soc. Chim. 33, 157, 395 (1905).
4. Ch. Mayer, Bull. Soc. Chim. 19, 427 (1916).
5. N. S. Kozlov, I. A. Shur, ZhOKh 29, 2706 (1959); N. S. Kozlov, Z. A. Abramova, DAN SSSR 132, 839 (1960); N. S. Kozlov, V. D. Pak, ZhOKh 30, 2400 (1960).
6. Sint. org. prep., sb. 2, 464 (1949).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

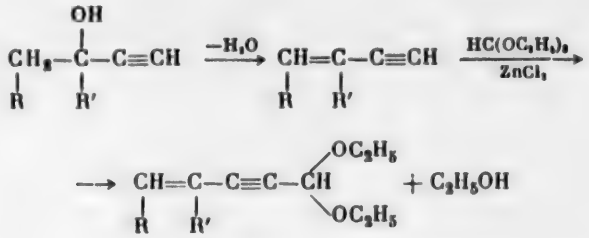
SYNTHESIS OF ACETALS OF VINYLACETYLENIC ALDEHYDES

V. B. Mochalin and N. G. Ivanova

The M. V. Lomonosov Moscow Institute of Fine Chemical Technology

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3896-3899, December, 1961
Original article submitted December 10, 1960

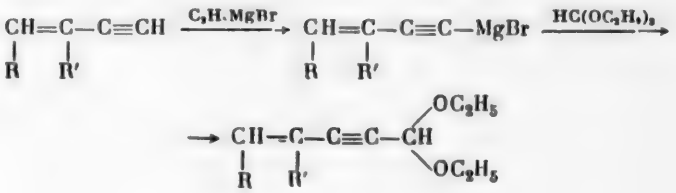
The acetals of vinylacetylenic aldehydes, like the aldehydes themselves, have hardly been studied at all up to the present time. There are only a few communications referring to compounds of this series [1]. In the present paper we shall describe the production of acetals of vinylacetylenic aldehydes by three different methods.



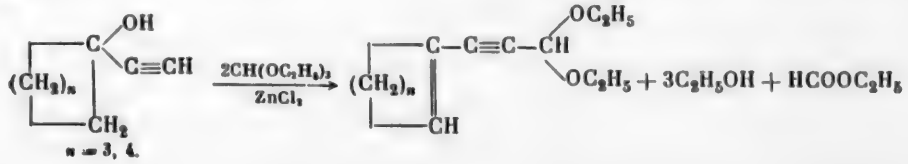
In method A, vinylacetylenic hydrocarbons were treated at 150-170° with orthoformic ester in the presence of catalytic amounts of zinc chloride. This method was recently proposed for the preparation of acetals of acetylenic aldehydes [2]. With low-boiling vinylacetylenic hydrocarbons, the reaction was carried out in sealed tubes. The acetals obtained consisted of colorless pleasant-smelling liquids which polymerize on standing. The constants and yields of the vinylacetylenic acetals are given in the table. The low yields of the diethyl acetals of pent-4-en-2-yn-1-al (I) and 4-methylpent-4-en-2-yn-1-al (II) are due to their ready polymerization during the reaction.

The initial vinylacetylenic hydrocarbons were prepared by dehydrating acetylenic alcohols with p-toluene sulfonic acid in acetic anhydride [3] or with phosphoryl chloride in pyridine [4].

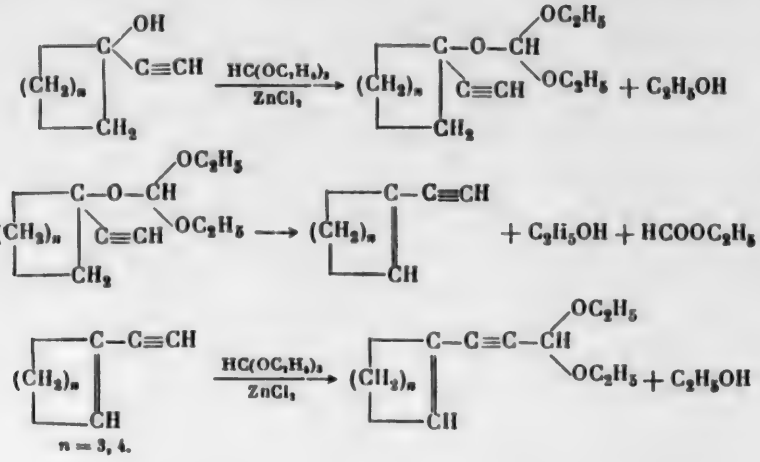
For comparison, all the acetals of the vinylacetylenic aldehydes were also obtained by the Grignard reaction (method B).



We found that ethylcyclopentanol and ethylcyclohexanol, when heated with a two-fold excess of orthoformic ester in the presence of zinc chloride, form acetals of the corresponding vinylacetylenic aldehydes (method C) by the following scheme:



The first stage of this reaction is, apparently, a transesterification with subsequent splitting out of a diethoxyformyl group, followed by the alkylation of the vinylacetylenic hydrocarbon by a second molecule of orthoformic ester. The end of the reaction is found from the amount of the mixture of ethanol and ethyl formate distilled off.



The 2,4-dinitrophenylhydrazones of the vinylacetylenic aldehydes, obtained directly from the acetals by treating them with an alcoholic solution of 2,4-dinitrophenylhydrazine in the presence of hydrochloric acid, were used to identify the acetals obtained by the different methods.

EXPERIMENTAL

The diethylacetal of pent-4-en-2-yn-1-al (I). Method A. A mixture of 55 g of orthoformic ester, 14.4 g of vinylacetylene, and 1 g of fused zinc chloride was heated in a thick-walled glass tube for 2.5 hours at 150-170°. After cooling, the contents of the tube were poured into a 10% solution of potash and extracted with ether. The ethereal extract was washed with water and dried with potash. The ether was distilled off, and the residue was distilled in vacuum. A yield of 4.2 g (10%) of the diethylacetal was obtained. The diethylacetals of 4-methylpent-4-en-2-yn-1-al (II) and of 4-t-butylpent-4-en-2-yn-1-al (III) were obtained by a similar procedure.

The diethylacetal of 3-(cyclopent-1'-en)-ylprop-2-yn-1-al (IV). Method A. A mixture of 9.2 g of 1-ethylcyclopent-1-ene, 14.82 g of orthoformic ester, and 1.5 g of fused zinc chloride was heated in a Favorskii flask at 125-155°. After 45 minutes, 6 ml of alcohol had distilled over. After cooling, the reaction mass was poured into a 10% solution of potash and extracted with ether. The ethereal extract was washed with water and dried with potash. The ether was distilled off, and the residue was distilled in vacuum. A yield of 10.5 g (54.5%) of the diethylacetal was obtained. The diethylacetal of 3-(cyclohex-1'-en)-yl-prop-2-yn-1-al (V) was obtained similarly.

The diethylacetal of 4-methylpent-4-en-2-yn-1-al (II). Method B. A solution of 22.2 g of isopropenylacetylene in 70 ml of absolute ether was added to the ethylmagnesium bromide obtained from 11.3 g of magnesium and 73.2 g of ethyl bromide in 100 ml of absolute ether, with stirring. The solution was heated for 3 days at 30-40°. After cooling to 0°, a solution of 69.5 g of orthoformic ester in 75 ml of ether was added. On the next day, the reaction mass was decomposed with 100 ml of a saturated solution of ammonium chloride. The ethereal layer was separated and the aqueous layer extracted with ether. The ethereal extract was dried with potash. The ether was distilled and the residue was distilled in vacuum. A yield of 25.4 g (46.5%) was obtained. The acetals (I), (III), (IV), and (V) were obtained by the same method.

The diethylacetal of 3-(cyclohex-1'-en)-ylprop-2-yn-1-al (V). Method C. A mixture of 18.6 g of 1-ethylcyclohexanol, 44.5 g of orthoformic ester, and 1.5 g of fused zinc chloride was heated in a Favorskii flask at 130-150°. After 2 hours 15 minutes, 34.5 ml of a mixture of ethanol and ethyl formate had distilled over. After cooling, the reaction mixture was poured into a 10% solution of potash and extracted with ether. The ethereal extract was washed with water and dried with potash. The ether was distilled, and the residue was distilled in vacuum. A yield of 10 g of (V) was obtained. The diethylacetal of 3-(cyclopent-1'-en)-ylprop-2-yn-1-al (IV) was obtained in a similar manner.

Comp. No.	R	R′	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	Found, %		Empirical formula	Calc. %		Yield (in %) by method			Analysis of the 2,4-dinitrophenyl-hydrazones			
						C	H		C	H	A	B	C	melting point	% N found	Empirical formula	% N calcu.
(I)	H	H	85° (20)	1.4508	0.9040	69.91	9.26	$C_9H_{14}O_2$	70.10	9.15	10	16.5	—	119.5°	21.39	$C_{11}H_8O_4N_4$	21.63
						70.09	9.32							120.5	21.45		
(II)	H	CH_3	98—99 (25)	1.4501	0.8910	71.45	9.84	$C_{10}H_{16}O_2$	71.39	9.59	16	46.5	—	139.5	20.60	$C_{12}H_{10}O_4N_4$	20.44
						71.43	9.82								20.36		
(III)	H	t-C_4H_9	115—117 (20)	1.4521	0.8820	74.48	10.79	$C_{13}H_{22}O_2$	74.24	10.54	46.2	45.5	—	130.5	17.41	$C_{15}H_{16}O_4N_4$	17.71
						74.11	10.81								17.66		
(IV)	$—CH_2CH_2CH_2—$		97 (2)	1.4774	0.9561	74.10	9.52	$C_{12}H_{18}O_2$	74.19	9.34	55	38	35	150	16.45	$C_{14}H_{12}O_4N_4$	16.66
						73.99	9.57								16.79		
(V)	$—CH_2CH_2CH_2CH_2—$		118 (3)	1.4872	0.9572	75.12	9.77	$C_{13}H_{20}O_2$	74.96	9.68	53.2	70	33	157—158	17.85	$C_{13}H_{14}O_4N_4$	17.82
						74.88	9.99								17.93		

SUMMARY

Acetals of vinylacetylenic aldehydes have been obtained by three different methods. A scheme for the production of vinylacetylenic acetals from 1-ethinyl-1-hydroxycycloalkanes has been proposed.

REFERENCES

1. A. Dornow, F. Ische, Ang. Chem. 67, 653 (1955); M. F. Shostakovskii, A. V. Bogdanova, G. I. Plotnikova, Izv. AN SSSR 1960, 1524; E. R. H. Jones, Z. Skattebol, M. C. Whiting, J. Chem. Soc. 1958, 1054.
2. B. W. Howk, J. S. Sauer, United States Patent No. 2,840,613; Ch. A. 52, 17186 (1958); J. Am. Chem. Soc. 80, 4607 (1958).
3. A. F. Thompson, E. N. Show, J. Am. Chem. Soc. 64, 363 (1942).
4. Kh. V. Val'yan, N. A. Borovikova, ZhOKh 29, 2882 (1959).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SYNTHESIS OF O-AMINOACYL DERIVATIVES OF ADENOSINE AND A STUDY OF THEIR PROPERTIES

É. Ya. Dreiman, V. A. Dmitrieva, S. G. Kamzolova, Z. A. Shabarova, and M. A. Prokof'ev

M. V. Lomonosov Moscow State University
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 3899-3905, December, 1961
Original article submitted November 3, 1960

In connection with the great significance pertaining to a number of biochemical conversions by an O-peptide (amino acid) derivative of adenylic acid, we undertook an investigation of convenient methods of synthesizing O-aminoacyl derivatives of adenosine and a study of some of their properties.

It was found possible to accomplish the synthesis of O-aminoacyl derivatives of adenosine by the action of cbz•-amino acids on free adenosine or its derivatives (5'-trityladenosine, 2':3'-isopropylideneadenosine) in the presence of dicyclohexylcarbodiimide in pyridine at room temperature. The reaction with free adenosine forms a 2' (or 3'),5'-di-O-aminoacyladenosine; the reaction with 5'-trityladenosine, depending on the molar ratios of the starting materials, forms either a mono-(2' or 3') derivative, or a 2',3'-di-O-aminoacyladenosine. A list of the compounds synthesized is given in the table.

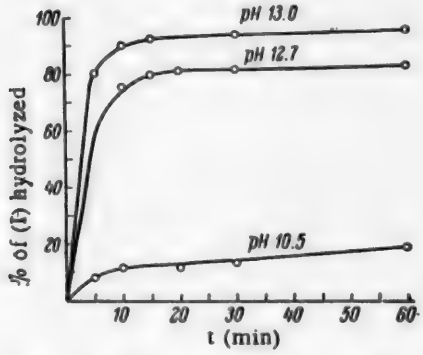


Fig. 1. Effect of time and pH of medium on hydrolysis of (I) at 20°.

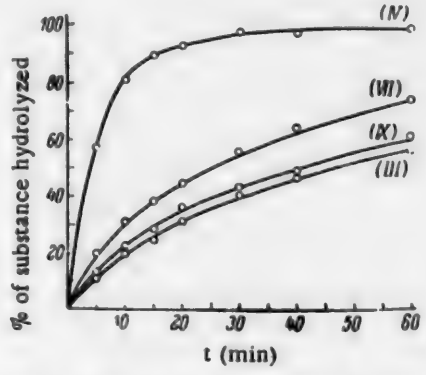


Fig. 2. Effect of time and nature of functional groups on the rate of hydrolysis of O-aminoacyl derivatives of adenosine (compounds III, IV, VII, and IX), pH 11.5, 20°.

An investigation of the hydrolysis of the compounds obtained showed that they are rather stable in acidic media and are hydrolyzed readily in alkaline media (see Figs. 1 and 2). For (I), the action of 0.1 N NaOH for 10-15 minutes at 20° is sufficient to attain practically complete hydrolysis of the compound with respect to the ester bond. Aminoacyl derivatives with an exposed NH_2 group are hydrolyzed more rapidly than compounds in which the amine group is protected. The position of the aminoacyl (2', 3', or 5') and also the nature of the aminoacyl (glycyl, phenylalanyl) does not have any great effect on the rate of hydrolysis.

•cbz = carbobenzoxy –

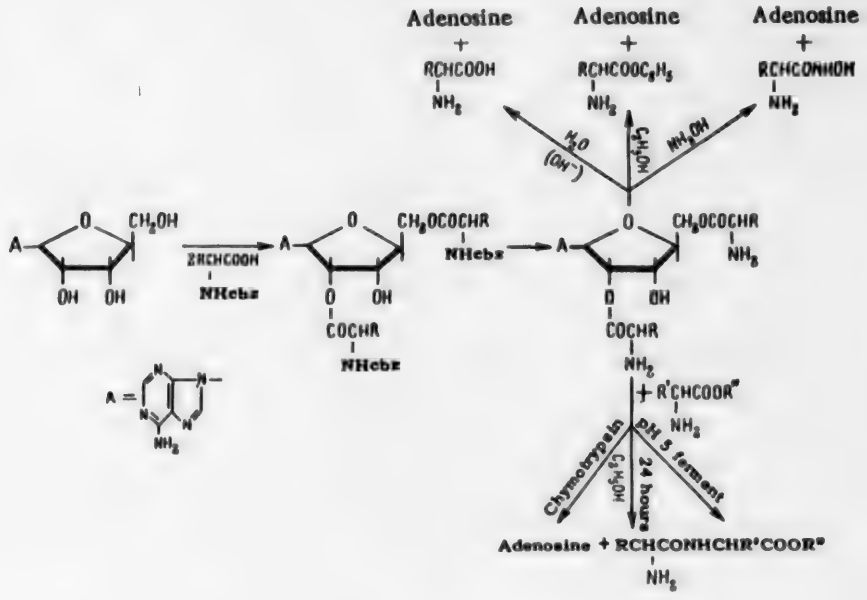
Comp. No.	Name of Compound	Yield (%)	Melting point (decomp.)	λ max in alcohol (mμ)	ε	R_f in syst. 1	Found %			Empirical Formula	Calculated %		
							C	H	N		C	H	N
(I)	2'(or 3'),5'-di-O-cbz-phenylalanyladenosine	70	88—92°	260	2990	0.87	63.61, 63.43	5.30, 5.32	11.60, 11.67	$C_{44}H_{43}O_{10}N_7$	63.70	5.20	11.82
(II)	2' (or 3'),5'-di-O-di-cbz lysyladenosine	45	216—218	253	2700	0.83	61.81, 61.70	5.70, 5.82	11.74, 11.79	$C_{54}H_{59}O_{14}N_9$	61.60	5.60	11.92
(III)	2',3'-isopropylidene-5'-O-cbz-phenylalanyladenosine	55	75—80	257—260	1620	0.90	61.79	5.98	14.69	$C_{30}H_{32}O_7N_6$	61.23	5.44	14.28
(IV)	2',3'-isopropylidene-5'-O-phenylalanyladenosine	43	55	260	4020	0.90	—	—	18.20, 17.99	$C_{22}H_{26}O_5N_6$	—	—	18.46
(V)	2'(or 3'),5'-di-O-phenylalanyladenosine	50	54	260	4200	0.87	59.93, 59.95	5.79, 6.02	17.51, 17.40	$C_{29}H_{31}O_6N_7$	59.89	5.52	17.46
(VI)	2'(or 3')-O-cbz-glycyl-5'-trityladenosine	48	80—85	—	—	—	—	—	11.72, 11.90	$C_{39}H_{36}O_7N_6$	—	—	12.00
(VII)	2'(or 3')-O-cbz-glycyladenosine	35	76—81	—	—	—	52.30	4.95	18.11	$C_{20}H_{22}O_7N_6$	52.40	4.80	18.34
(VIII)	2' (or 3')-O-cbz-phenylalanyl-5'-trityladenosine	50	75—80	—	—	—	70.01	5.33	10.35	$C_{46}H_{42}O_7N_6$	69.87	5.35	10.63
(IX)	2',3'-di-O-cbz-phenylalanyladenosine	36	71—76	—	—	0.86	63.32	5.28	11.87	$C_{44}H_{43}O_{10}N_7$	63.69	5.22	11.81

Hydroxylamine reacts readily with the O-aminoacyl derivatives of adenosine, forming hydroxamates of the corresponding amino acids and adenosine. The hydroxamic reaction under the conditions of Lipmann [1] goes so readily that it can be used as a method of quantitative determination of the complex ester derivatives that we synthesized. We used the hydroxamic reaction to characterize the rate of hydrolysis of these compounds.

The O-aminoacyl derivatives of adenosine can be considered as unusual activated esters of amino acids in which a nucleoside has been introduced into the alcohol component of the ester as an electrophilic activating substituent. Such "activated" complex esters are capable of peptide synthesis reactions [2].

Compound (V), interacting with the ethyl ester of glycine for 24 hours, forms the ethyl ester of phenylalanylglycine. That same compound in phosphate buffer at pH 8 in the presence of chymotrypsin forms the ester of the dipeptide in a short time (up to two hours). The ethyl ester of the dipeptide is also formed if the reaction of (V) with the phenylalanine ester is conducted in the presence of ferment extract from liver homogenate (so-called "pH 5 ferment") [3].

The scheme of synthesis and conversions of O-aminoacyladenosines may be represented in the following form:



EXPERIMENTAL

Systems for Chromatography:

n-Butyl alcohol saturated with water (system 1); n-butyl alcohol – water – acetic acid (4:4:1) (system 2); isoamyl alcohol – 5% Na_2HPO_4 (system 3); n-butyl alcohol saturated with NH_3 (system 4).

I. Synthesis of O-Aminoacyl Derivatives of Adenosine

Compound (I). To a solution of 0.8 g (0.001 mole) of adenosine and 2.7 g (0.003 mole) of cbz-phenylalanine in 5 ml of absolute pyridine, 1.9 g (0.003 mole) of dicyclohexylcarbodiimide was introduced. After standing for a day, the precipitate was filtered off, and the solution was evaporated to dryness. The remaining oil was dissolved in chloroform and washed with 10% acetic acid, saturated sodium bicarbonate solution, and water. Dried over $MgSO_4$. Evaporated to a small volume (2 ml) and recovered compound (I) by addition of petroleum ether. Purified by recrystallization from CCl_4. The constants, yields, and analytical data on compound (I) and the other O-aminoacyl derivatives of adenosine (II-IX) are listed in the table.

Compound (II). Obtained analogously, from 0.27 g adenosine and 1.24 g di-cbz-lysine. Purified by recrystallization from alcohol.

Compound (III). Obtained analogously, from 0.31 g 2':3'-isopropylideneadenosine and 0.9 g cbz-phenylalanine. Purified by reprecipitation from chloroform by petroleum ether.

Compound (IV). To a solution of 0.25 g of (III) in 90% acetic acid, cooled to 0°, freshly prepared Pd catalyst was added. Reduction with a stream of hydrogen was continued about one hour. After removal of the catalyst, the solution was subjected to lyophilic drying. The compound was purified by precipitation from chloroform solution by petroleum ether.

Compound (V). From 0.25 g of (I) by reduction over Pd catalyst, as indicated for (IV).

Compound (VI). From 0.5 g (0.001 mole) of trityladenosine, 0.1 g (0.001 mole) of cbz-glycine, and 0.082 g (0.0015 mole) of dicyclohexylcarbodiimide in absolute pyridine, as indicated for (I). Purified by recrystallization from carbon tetrachloride.

Compound (VII). To a solution of 70 mg of (VI) in 2 ml absolute chloroform, added 15 ml absolute chloroform saturated at 0° with dry HCl. After 20 minutes, the reaction mixture was washed with saturated $NaHCO_3$ solution and with water. The solution was dried over $MgSO_4$ and evaporated under vacuum to a small volume, and the (VII) was precipitated by petroleum ether. Purified by reprecipitation.

Compound (VIII). Obtained analogously to (VI) from 0.36 g trityladenosine, 0.18 g cbz-phenylalanine, and 0.14 g dicyclohexylcarbodiimide in 10 ml absolute pyridine.

Compound (IX). From 2.04 g trityladenosine, 2.99 g cbz-phenylalanine, and 2.1 g dicyclohexylcarbodiimide in absolute pyridine, obtained in 48 hours 3.3 g of 2',3'-di-O-cbz-phenylalanyl-5'-trityladenosine (X). Purified by reprecipitation from chloroform by petroleum ether.

From 1 g of (X), by treatment with HCl-saturated chloroform, obtained (IX). Purified by reprecipitation from chloroform.

II. Reaction of O-Aminoacyl Derivatives of Adenosine with Hydroxylamine

To 2 ml alcoholic solution of 2 mg of (I), added 2 ml hydroxylamine in NaOH (25 ml of 2 N $NH_2OH \cdot HCl$ + 15 ml 4 N NaOH), allowed to stand 15 minutes, and chromatographed in system 2. The chromatogram was developed with a 10% solution of $FeCl_3$ in methyl alcohol. Detected a spot with $R_f = 0.96$, coinciding with the control spot of cbz-phenylalanine hydroxamate. In the quantitative determination of the hydroxamate formed (see below) it was found that the cbz-phenylalanyl residue reacted completely with the hydroxylamine. In the interaction of (IV) and (V) with hydroxylamine, phenylalanine hydroxamate was detected ($R_f = 0.63$ in the same system).

III. Hydrolysis of O-Aminoacyl Derivatives of Adenosine

Hydrolysis of (I). A 20-mg quantity of(I) was dissolved in 1 ml alcohol, and there was added 9 ml alcoholic-buffer solution pH 10.5 (4.5 ml alcohol and 4.5 ml phosphate buffer). Samples (1 ml) were withdrawn at 0, 5, 10, 15, 20, 30, 40, 60, and 120 minutes. There was added to the sample 2 ml alcohol, and then 4 ml hydroxylamine solution (prepared before the experiment by mixing 25 ml of 2 N $NH_2OH \cdot HCl$ and 15 ml of 4 N NaOH). After standing 10 minutes, there was added to the solution 4 ml of 5% CCl_3COOH solution, 1 ml of 10% HCl, and 3 ml of a 10% solution of $FeCl_3$ in 0.1 N HCl. The solution was analyzed colorimetrically on an "FÉK-M" photocolorimeter at 535 mμ. Based on a calibration curve plotted specially for cbz-phenylalanine hydroxamate, the concentration of the latter in the solution was determined. The amount of amino acid hydroxamate present in the solution (120 minutes) was equivalent to its quantity in the (I).

The relation between hydrolysis rate and time and pH is presented in Fig. 1. The hydrolysis does not go in 0.1 N HCl, nor at pH 7.75 or 9.24.

Hydrolysis of (III), (IV), (VII), and (IX) was studied at pH 11.5, by methods analogous to the preceding. The experimental data are shown in Fig. 2.

Hydrolysis of (V). A solution of 10 mg of (V) in 2 ml alcohol was diluted with 5 ml water and allowed to stand at room temperature for 24 hours. Then the reaction mixture was chromatographed in system 1. Detected a spot with $R_f = 0.27$ (adenosine) and $R_f = 0.52$ (phenylalanine). The spot with $R_f = 0.87$ (V) disappeared.

Alcoholysis of (I) and (IV). A 10-mg quantity of (I) or (IV) was dissolved in 5 ml alcohol and left 3 days at room temperature. The solution was chromatographed in system 1. A spot was detected with R_f = 0.70 (ethyl ester of phenylalanine), developed with ninhydrin.

IV. Peptide Synthesis with the Participation of O-Aminoacyl Derivatives of Adenosine

Formation of Dipeptides with Ethyl Ester of Glycocoll. A solution of 0.052 g of (V) and 0.1 g of the ethyl ester of glycocoll in 10 ml of anhydrous alcohol was left 24 hours at room temperature. After evaporation, the reaction mixture was chromatographed in system 1. Detected the ethyl ester of phenylalanylglycine (R_f = 0.73).

For a proof of the structure, the substance with R_f = 0.73 was hydrolyzed with 6 N HCl, 5 hours at 100°. On the chromatogram in system 1, detected phenylalanine (R_f = 0.52) and glycine (R_f = 0.17). In control experiments, when compound (V) was replaced by phenylalanine or its methyl ester, formation of the dipeptide did not occur.

An analogous reaction was carried out with compound (VI). Before chromatographing, the reaction mixture was evaporated and the residue was heated 60 minutes at 100° with 10% acetic acid. On chromatography in system 1, detected the ethyl ester of phenylalanylglycine (R_f = 0.73), the eluate of which after hydrolysis gave phenylalanine and glycine.

Formation of Dipeptides with Esters of Amino Acids in the Presence of Chymotrypsin. To 55 mg of (I) in 2 ml of alcohol, added 100 mg of the hydrochloride of the ethyl ester of glycocoll in 0.5 ml water, 0.3 ml of 2 N NaOH, 9 ml of phosphate buffer solution (pH 8), and 9 mg of crystalline chymotrypsin in several portions. The suspension was shaken 2 hours, then diluted to 50 ml with water; the precipitate was removed and dried, and several milliliters of glacial CH_3COOH saturated with HBr was added. After 1 hour, ether was added. The oil separated. By means of paper chromatography in system 2, there was recovered 7 mg of the ethyl ester of phenylalanylglycine (R_f = 0.73). In the filtrate of the reaction mixture, adenosine was detected chromatographically (R_f = 0.27 in system 1 and R_f = 0.55 in system 3).

For establishing the structure of the dipeptide, it was treated for 1 hour with 1 N NaOH and then hydrolyzed with 6 N HCl for 12 hours at 100°. Detected glycocoll (R_f = 0.17 in system 2) and phenylalanine (R_f = 0.50 in system 2).

The order of the amino acids in the dipeptide was determined by the dinitrophenyl method [4]. Detected DNF-phenylalanine [DNF = dinitrophenyl.] (R_f = 0.79 in system 4, λ_{max} 360 mμ) and glycocoll. In an experiment conducted analogously but without chymotrypsin, no dipeptide was detected.

The interaction of compounds (IV) and (V) with the ethyl ester of glycocoll under analogous conditions gave the ethyl ester of phenylalanylglycine and adenosine (chromatographic determination).

Formation of Dipeptides with Esters of Amino Acids in the Presence of "pH 5 Ferment." To a solution of 52 mg of (V) in 20 ml of phosphate buffer (pH 7.5), a solution of 100 mg of the ethyl ester of glycine in 5 ml of the same buffer was added. To the mixture there was added 0.2 ml of "pH 5 ferment," recovered from liver homogenate. The mixture was left for 24 hours at room temperature. Then the solution was evaporated to dryness. The residue was extracted with alcohol. The alcoholic solution was evaporated and chromatographed in system 2. Detected a spot with R_f = 0.73 (ethyl ester of phenylalanylglycine). The ester of the dipeptide was recovered by means of preparative chromatography, and its composition was determined after hydrolysis with 6 N HCl at 100° for 5 hours. On the chromatogram in system 2, detected phenylalanine (R_f = 0.52) and glycine (R_f = 0.17). In a control experiment (without the "pH 5 ferment") no dipeptide formation was observed.

SUMMARY

1. A method has been developed for the synthesis of O-aminoacyl derivatives of adenosine, based on the interaction of adenosine or its derivatives with N-carbobenzoxyamino acids in the presence of dicyclohexylcarbodiimide.

2. A study has been made of the hydrolytic stability of O-aminoacyl derivatives of adenosine. In acidic media they are not hydrolyzed; the rate of hydrolysis increases as the hydrogen ion concentration in the solution is decreased. The compound is subject to alcoholysis.

3. The interaction of O-aminoacyl derivatives of adenosine with NH_2OH goes rapidly and quantitatively. The reaction can serve as a measure for the quantitative determination of these compounds in solution.

4. A study has been made of the reaction of peptide formation of O-aminoacyl derivatives of adenosine with esters of amino acids. This reaction occurs especially readily in the presence of chymotrypsin and "pH 5 ferment" (a group of ferments recovered from liver homogenate). It has been established that in O-aminoacyl derivatives of adenosine the ester bond is activated by the nucleoside.

LITERATURE CITED

1. W. Lipmann, J. Am. Chem. Soc. 59, 2308 (1937).
2. R. Schwyzer, B. Iselin, W. Rittel, P. Sieber, Helv. Chim. Acta. 39, 872 (1956); B. Iselin, R. Schwyzer, Helv. Chim. Acta. 39, 57 (1956).
3. M. Hoagland. Biochim. Biophys. Acta. 16, 288 (1955).
4. F. Sanger, Biochem. J. 38, 507 (1945).

RESEARCH IN THE FIELD OF GLYCOL ETHERS AND THEIR DERIVATIVES

XXXIX. SYNTHESIS OF AROMATIC γ-CHLOROETHERS

Shamkhal Mamedov and D. N. Khydyrov

Institute of Petrochemical Processes, Academy of Sciences, Azer. SSR
Translated from Zhurnal Obshchei Khimii Vol. 31, No. 12,
pp. 3905-3909, December 1961
Original article submitted August 22, 1960

It was shown previously that aliphatic γ-haloethers are obtained readily by the alkoxymethylhalogenation of ethylenic hydrocarbons by α-haloethers [1]. Some of the γ-chloroethers that were synthesized proved to be highly effective insecticides [2], acaricides [3], and herbicides [4].

It was of interest to study the possibilities of synthesizing γ-chloroethers by the alkoxymethylchlorination of styrene by α-chloroethers; based on information in the literature, such possibilities have not been investigated.

Our experiments showed that α-chloroethers under alkoxymethylchlorination conditions react smoothly with styrene, giving aromatic γ-chloroethers (I) with good yields (60-75%).

$$C_6H_5-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-O-R \quad (I)$$

R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11}, iso-C_5H_{11}.

The γ-chloroethers (I) under the usual conditions readily give organomagnesium compounds (II), which on decomposition with water lead to the formation of ethers of hydrocinnamyl alcohol (III) with yields of 60-67%. These ethers have a pleasant, delicate odor, which may find them applications in the perfume industry.

$$C_6H_5-\underset{\underset{C_6H_5-CH-CH_2-CH_2-O-R}{|}}{CH}-CH_2-CH_2-O-R \quad (IV)$$

$$C_6H_5-CH-CH_2-CH_2-O-R \xleftarrow{} C_6H_5-\underset{\underset{MgCl}{|}}{CH}-CH_2-CH_2-O-R \quad (II) \xrightarrow{H_2O}$$

$$\longrightarrow C_6H_5-CH_2-CH_2-CH_2-O-R \quad (III)$$

In the preparation of compound (II) from (I) it is necessary to establish suitable conditions by means of thorough cooling of the reaction mixture and relatively slower addition of (I) to the metallic magnesium, which makes it possible to avoid almost completely the parallel anomalous reaction course toward the formation of the product (IV) of the Wurtz-Fittig reaction.

The action of alcoholic caustic on (I) leads to splitting out the elements of hydrogen chloride, and cinnamyl alcohol ethers (V) are obtained with good yields (80%). The cinnamyl alcohol ethers have a pleasant floral odor [5], and the scheme indicated above for their synthesis may open a convenient route to a wider introduction of these most valuable organic compounds into the perfume industry.

The ethers (V) behave as unsaturated compounds, and their bromination proceeds smoothly with the formation of a dibromoether (VI) with yields of 80%.

By the action of potassium acetate on (I) in glacial acetic acid medium, mixed ester-ethers (VII) are obtained: the saponification of these compounds leads to the formation of partial ethers of aromatic 1,3-diols (VIII) with 85% yield.

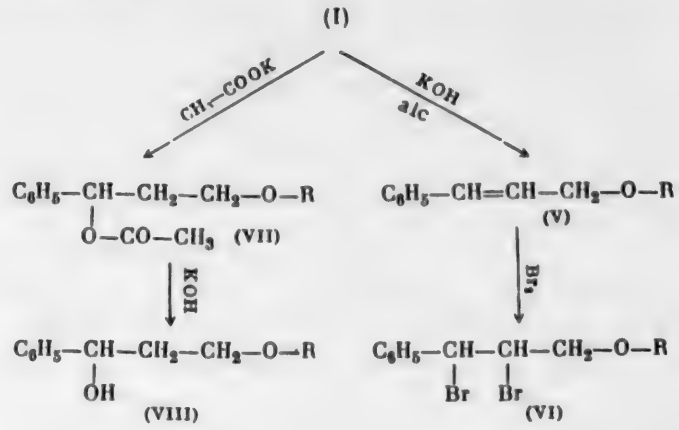
TABLE 1. Aromatic γ-Chloroethers (I) $C_6H_5-CHCl-CH_2-CH_2-OR$

Comp. No.	R	Empirical formula	B.p. (pressure, mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	% C found	% C calc.	% H found	% H calc.	% Cl found	% Cl calc.	Yield (in %)
1	CH_3	$C_{10}H_{13}OCl$	100—101.5° (6)	1.0791	1.5168	51.70	51.29	65.44, 65.34	65.04	7.17, 7.16	7.05	18.81, 19.64	19.24	75
2	C_2H_5	$C_{11}H_{15}OCl$	106—107 (6)	1.0535	1.5108	56.43	55.91	66.85, 66.30	66.50	7.82, 7.76	7.56	18.09, 17.70	17.88	73
3	n-C_3H_7	$C_{12}H_{17}OCl$	123—123 (7)	1.0334	1.5038	60.87	60.53	67.92, 67.46	67.76	8.18, 8.12	8.00	17.05, 16.98	16.71	70
4	iso-C_3H_7	$C_{12}H_{17}OCl$	113—114 (5)	1.0226	1.5002	61.14	60.53	67.89, 67.94	67.76	8.21, 7.92	8.00	17.00, 16.94	16.71	70
5	n-C_4H_9	$C_{13}H_{19}OCl$	133—134 (7)	1.0207	1.5015	65.44	65.15	69.00, 68.65	68.87	8.15, 8.26	8.39	16.10, 15.95	15.67	60
6	iso-C_4H_9	$C_{13}H_{19}OCl$	122—124 (5)	1.0102	1.4976	65.67	65.15	68.86, 68.78	68.87	8.56, 8.48	8.39	15.58, 15.68	15.67	60
7	n-C_5H_{11}	$C_{14}H_{21}OCl$	140—142 (2)	1.0088	1.4992	70.02	69.76	70.12, 69.97	69.85	8.86, 8.91	8.73	14.55, 14.90	14.76	50
8	iso-C_5H_{11}	$C_{14}H_{21}OCl$	138—139.5 (6)	1.0038	1.4972	70.13	69.76	70.08, 69.95	69.85	8.84, 8.80	8.73	14.48, 14.62	14.76	58

TABLE 2. Ethers of Cinnamyl and Hydrocinnamyl Alcohol

Comp. No.	Structural formula of ethers	Empirical formula	B. P. (pressure mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	% C found	% C calc.	% H found	% H calc.	Yield (in %)
1	$C_6H_5-CH=CH-CH_2-OCH_3$	$C_{10}H_{12}O$	100—101° (10)	0.9737	1.5344	47.27	47.06	80.75, 80.98	81.08	8.34, 8.21	8.11	81
2	$C_6H_5-CH=CH-CH_2-OC_3H_7$-iso	$C_{12}H_{16}O$	89—90 (2)	0.9458	1.5196	56.53	56.29	81.68, 81.72	81.82	9.22, 9.18	9.09	78
3	$C_6H_5-CH_2-CH_2-CH_2-OC_3H_7$-iso	$C_{12}H_{18}O$	89 (3)	0.9064	1.4840	56.18	55.66	80.98, 81.06	80.90	10.27, 10.22	10.11	67
4	$C_6H_5-CH_2-CH_2-CH_2-OC_4H_9$-iso	$C_{13}H_{20}O$	111—113 (10)	0.8998	1.4820	60.83	60.28	81.05, 81.12	81.25	10.61, 10.56	10.42	60

However, an attempt to obtain these monoethers (VIII) by direct hydrolysis of the γ-chloroethers (I) did not give favorable results, since at the same time HCl is split out, forming ethers of cinnamyl alcohol (V); this is in agreement with previous observations [1].



Biological tests conducted in our laboratory showed that the aromatic γ-chloroethers (I) possess physiological activity. Some of them are highly effective insecticides against cotton pests [6]. In addition, they proved to be suitable components for formulating new toxic chemicals against bollworms [7].

EXPERIMENTAL

Methyl γ-Chloro-γ-phenylpropyl Ether (I, R = CH_3). To a mixture of 80.5 g α-chloromethyl methyl ether, 100 g CCl_4, and 1.21 g anhydrous $ZnCl_2$ (1.5% of the α-chloroether weight), 104 g styrene (dissolved in 100 g CCl_4) was added dropwise over 2 hr, stirring and cooling (15-20°). Stirring was continued 2 hr more at this temperature. Then the contents of the flask were decomposed with water, and the reaction product (bottom layer) was washed with 3% NaOH and with water (two times each). After drying and driving off the solvent, distillation gave 138.5 g (75% based on styrene weight) of the ether (I, R = CH_3), an oily liquid with a pleasant ethereal odor (Table 1, compound 1).

The other seven new γ-chloroethers were obtained under analogous conditions; their constants are listed in Table 1.

Action of Alcoholic Caustic on Methyl γ-Chloro-γ-phenylpropyl Ether (I, R = CH_3). To a mixture of 207 g alcohol an 84 g powdered KOH, 92.25 g of the γ-chloroether (I, R = CH_3) was added. The reaction flask was heated in a water bath (80-90°) 8 hr with continous stirring. Then the alcohol was distilled off, and water was added to the residue until the sediment was completely dissolved. The reaction product was extracted with ether. After washing, drying, and driving off the solvent, there was recovered by distillation 60 g (81%) of the methyl ether of cinnamyl alcohol (V, R = CH_3) (Table 2, compound 1).

Isopropyl Ether of Cinnamyl Alcohol (V, R = iso-C_3H_7). From 42 g solid KOH, 100 g alcohol, and 54 g of the γ-chloroether (I, R = iso-C_3H_7), under the conditions of the preceding experiment, obtained 34.5 g (78%) of the ether (V, R = iso-C_3H_7) (Table 2, compound 2).

Action of Bromine on Methyl Ether of Cinnamyl Alcohol (V, R= CH_3). To a mixture of 59.2 of the ether (V, R = CH_3) and 200 ml absolute ether, 64 g bromine was added with cooling (0°) and stirring. Then stirring was continued 3 hr at the same temperature. After washing (Na_2CO_3, H_2O), drying with Na_2SO_4, and driving off the solvent, there was obtained by vacuum distillation 99 g (80%) of the ether (VI, R = CH_3).

B.p. 150-151° (8 mm), d_4^{20} 1.6378, n_D^{20} 1.5788, MR_D 62.47. $C_{10}H_{12}OBr_2$ F_3. Calculated 61.95.

This product crystallized in storage; m.p. 45-46.5° (from alcohol).

Found %: C 39.12, 39.25; H 3.78, 4.04; Br 52.36, 51.76. $C_{10}H_{12}OBr_2$. Calculated %: C 38.96; H 3.90; Br 51.95.

Isopropyl Ether of Hydrocinnamyl Alcohol (III, R = iso-C_3H_7). From 21.2 g metallic magnesium and 187 g isopropyl γ-chloro-γ-phenylpropyl ether (I, R = iso-C_3H_7) in a medium of 250 ml absolute ether, the organomagnesium compound (II, R = iso-C_3H_7) was prepared by the usual method. On the following day, 400 ml of acidified water was added to the well-cooled mixture. After washing, drying, and driving off the solvent, obtained 105 g (67%) of the isopropyl ether of hydrocinnamyl alcohol (III, R = iso-C_3H_7) (Table 2, compound 3) and 20 g (12.8%) of α,α'-diisopropoxy-γ,γ'-diphenylbutane (IV, R = R = iso-C_3H_7); white crystals, m.p. 86-87° (from alcohol).

Found%: C 80.98; 81.11; H 9.99, 9.75. $C_{24}H_{24}O_2$. Calculated %: C 81.35; H 9.60.

Isobutyl Ether of Hydrocinnamyl Alcohol (III, R = iso-C_4H_9). From 24 g magnesium, 226.5 g isobutyl γ-chloro-γ-phenylpropyl ether (I, R = iso-C_4H_9), and 350 ml absolute ether, the organomagnesium compound (II, R = iso-C_4H_9) was prepared, and then decomposed with acidified water. By the usual operation, recovered 116 g (60%) of the ether of hydrocinnamyl alcohol (III, R = iso-C_4H_9) (Table 2, compound 4).

Action of Potassium Acetate on Isopropyl γ-Chloro-γ-phenylpropyl Ether (I, R = iso-C_3H_7). To a mixture of 98 g anhydrous potassium acetate and 200 ml glacial acetic acid, there was added 127.5 g of the ether (I, R = iso-C_3H_7), and the reaction mixture was heated (90-100°) 12 hr with stirring. Then water was added to the flask, and the reaction product was extracted with ether. After washing, drying, and driving off the solvent, recovered 85.5 g (60%) α-phenyl-γ-isopropoxypropyl acetate (VII, R = iso-C_3H_7).

B.p. 108-109.5° (2 mm), d_4^{20} 1.0102, n_D^{20} 1.4840, MR_D 66.84. $C_{14}H_{20}O_3F_3$. Calculated 66.55.
Found %: C 71.44, 71.36; H 8.54, 8.31. $C_{14}H_{20}O_3$. Calculated %: C 71.19; H 8.48.

Saponification of Ester (VII, R = iso-C_3H_7). To a mixture of 59 g of the ester (VII, R = iso-C_3H_7) and 100 ml methanol, there was added a solution of 16 g NaOH in 200 ml distilled water. Then the reaction mixture was heated in a water bath (50-55°) 4 hr with stirring and then diluted with water, and the reaction product was extracted with ether. After drying and driving off the solvent, obtained 49 g of oily liquid, from which by vacuum distillation was obtained 42.7 g (88%) of the isopropyl monoether of the aromatic 1,3-diol (VIII, R = iso-C_3H_7).

B.p. 115-116.5° (4 mm), d_4^{20} 0.9981, n_D^{20} 1.5005, MR_D 57.21. $C_{12}H_{18}O_2F_3$. Calculated 57.18.
Found %: C 73.88, 73.99; H 9.39, 9.32. $C_{12}H_{18}O_2$. Calculated %: C 74.23; H 9.28.

SUMMARY

1. A study has been made of the reaction of alkoxymethylchlorination of styrene by α-chloroethers in the presence of $ZnCl_2$.

2. Fifteen new aromatic ethers have been synthesized and investigated.

3. A convenient method of synthesis has been proposed for ethers of cinnamyl alcohol.

4. A preparative method has been proposed for the synthesis of ethers of hydrocinnamyl alcohol.

5. It has been established that aromatic γ-chloroethers possess insecticidal properties.

LITERATURE CITED

1. Shamkhal Mamedov, ZhOKh 27, 1499 (1957).
2. Shamkhal Mamedov, Kh. M. Alieva, O. B. Osipov and A. R. Mamedova. Author's certificate, Sept. 7, 1957, No. 111627.
3. Shamkhal Mamedov, A. R. Mamedova, A. A. Alieva, O. B. Osipov, Author's certificate, Aug. 19, 1959, No. 128117; "Byull. izobret," No. 9 (1960).
4. Shamkhal Mamedov, O. B. Osipov and V. M. Zeinalova, Author's certificate, Aug. 7, 1959, No. 128683; "Byull. izobret." No. 10 (1960).
5. V. I. Isagulyants, Synthetic Perfumes [in Russian] Erevan, 796 (1947).
6. Shamkhal Mamedov, D. N. Khydyrov, A. S. Agaev, O. B. Osipov, E. N. Grishina, Author's certificate, Oct., 15, 1959, No. 132911; "Byull. izobret." No. 20 (1960).
7. Shamkhal Mamedov, A. S. Agaev, D. N. Khydyrov, O. B. Osipov, A. G. Pishnamazov, Author's certificate, Oct. 31, 1959, No. 131589; "Byull. izobret," No. 17 (1960).

2,5-DIMETHOXY-2,5-DIHYDROFURFURYL BENZOATES AND SOME OF THEIR REACTIONS

N. K. Kochetkov, L. I. Kudryashov, N. V. Molodtsov, and E. D. Khomutova

Institute of the Chemistry of Natural Compounds, Academy of Sciences, USSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 3909-3916, December, 1961
Original article submitted January 20, 1961

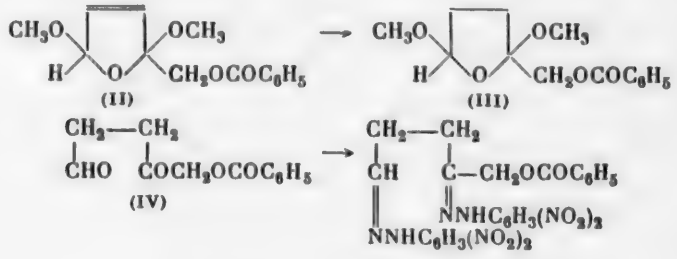
Despite the large number of studies devoted to the alkoxylation of furan homologs, there are very few analogous reactions for its derivatives containing functional groups, and these relate mainly to the methoxylation of esters of pyromucic acid [1-5], and also the acetal of furfurole [6] and N-benzoylfurfurylamine [7]; there is also information on the alkoxylation of furfuryl alcohol [6] and of its acetate [8].

In connection with a search for means of synthesizing polyhydroxy carbonyl compounds related to carbohydrates, we studied the methoxylation furfuryl benzoate and some conversions of the methoxylated products that were obtained.

In the methoxylation of furfuryl benzoate (I) under conditions analogous to those in the methoxylation of N-benzoylfurfurylamine [7], we recovered two methoxylated products that were identical in composition: crystalline (IIa) with m.p. 76-77° (yield 60%) and liquid (IIb) (yield about 20%); the latter was obtained by high-vacuum distillation of the oily residue remaining after removal of the solid isomer.

The results of the oxidation of these isomers, which were identical for both substances, show that they are geometric isomers of 2,5-dimethoxy-2,5-dihydrofurfuryl benzoate (trans and cis); subsequent work was performed mainly with the solid isomer (IIa).

To confirm the structure of these compounds, the solid isomer was hydrogenated on palladium, and the resulting tetrahydro derivative (III) was subjected to acid hydrolysis. The formation of ω-benzoyloxylevulinaldehyde (IV) (identified in the form of its bis-2,4-dinitrophenylhydrazone) as a result of this hydrolysis demonstrates that the starting material was actually 2,5-dimethoxy-2,5-dihydrofurfuryl benzoate.



We studied further the possibility of hydroxylation of the double bond in the isomeric benzoates (IIa) and (IIb); however, it was found that the double bond in both isomers is distinguished by unusual stability of hydroxylating agents. Negative results were obtained in the interaction of (IIa) and (IIb) with lead tetraacetate [9], iodine, and silver benzoate [10], in an attempt to introduce the iodhydrin grouping by the action of iodine in the presence of mercuric oxide and water [11], and in an oxidation according to Wagner.

Interesting results were obtained in the oxidation of the isomeric methoxylated products by performic acid. While perbenzoic and perphthalic acids do not oxidize either (IIa) or (IIb), both isomers reacted with performic acid,

although the reaction proceeds slowly. The interaction of the solid isomer (IIa) with performic acid results in the formation of two isomeric crystalline substances of composition $C_{12}H_{10}O_5$ having m.p. 172° (Va) and 101-103° (Vb), respectively. When the reaction is conducted at −10 to −20°, the high-melting isomer (Va) is formed preferentially, and at room temperature the low-melting isomer (Vb) is formed almost exclusively.

The composition and properties of the isomeric products of the oxidation indicatated that they were not epoxy derivatives nor products of further conversions of the latter. Both isomers were soluble in alkalies and were readily recovered from alkaline solutions in the form of their S-benzylisothiuronium salts; thus, they could be acids or lactones. On catalytic hydrogenation of both of the isomers (Va) and (Vb), one mole of hydrogen was absorbed, and one and the same hydrogenated derivative (VI) was formed, containing a carboxyl group; this was confirmed by the results of titration and by the formation of an S-benzylisothiuronium salt.

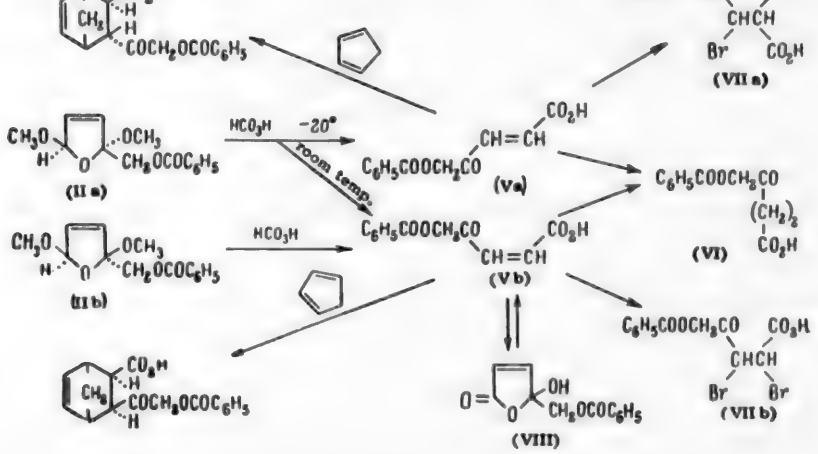
Both oxidation products (Va) and Vb) readily add one mole of bromine, being converted to two isomeric dibromides of composition $C_{12}H_{10}O_5Br_2$ (VIIa) and (VIIb) with similar properties. Finally, it should be pointed out that (Va) and (Vb) enter readily into the diene synthesis reaction with cyclopentadiene, forming two different adducts. In the IR spectrum of the high-melting isomer (Va), bands are detected corresponding to the hydrogen bond (3400 cm^{-1}), benzoyl group (1727 cm^{-1}), and conjugated carbonyl group (1690 cm^{-1}); in the spectrum of the low-melting isomer (Vb), there were absorption bands of alcoholic hydroxyl (3330 cm^{-1}), five-membered lactone (1767 cm^{-1}), and carbonyl group (1704 cm^{-1}). The IR spectrum of the dihydro derivative contains absorption bands of the hydrogen bond (3400 cm^{-1}), nonconjugated carbonyl group (1702 cm^{-1}), and carboxyl group (1716 cm^{-1}).

A comparison of all these data leads to the conclusion that the isomers (Va) and (Vb) are the two 5-benzoyloxy-4-ketopentene-2-oic acids. On the basis of the data of the IR spectra, of the differences in the melting points, and also of a detailed comparison of their conversion products, the high-melting isomer (Va) should be considered as the trans-isomer and the low-melting (Vb) as the cis-isomer. The hydrogenation product is 5-benzoyloxy4-ketopentanoic acid (VI).

Attention is drawn by the differences in the IR spectra of the isomeric unsaturated keto-acids (Va) and (Vb); these differences exceed the limits of the difference shown by geometric isomers. Evidently these differences, and expressly the presence of a band in the (Va) spectrum characteristic for a hydrogen bond and the presence of bands in the (Vb) spectrum characteristic for an alcoholic hydroxyl and a γ-lactone ring (without any hydrogen-bond absorption band), should be explained by the fact that the cis-isomer (Vb) exists to a considerable extent (if not completely) in the cyclic lactol form (VIII), in tautomeric ratios with the open form (Vb). It is natural that ring-chain tautomerism of this type, which is well known in other examples [12, 13], is not possible for the trans-isomer (Va) from purely geometric considerations.

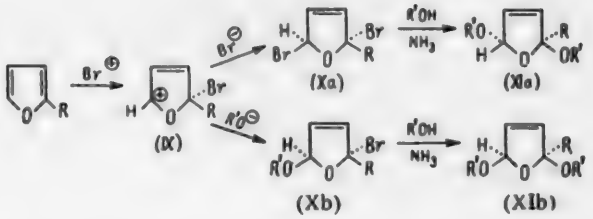
In the oxidation of the liquid isomer (IIb) by performic acid under analogous conditions, only compound (Vb) was obtained with good yield. The recovery in this case of a compound identical with the product of oxidation of the solid isomer (IIa) is thorough proof that the two isomers obtained on methoxylation (IIa) and (IIb) have one and the same structure, formed as a result of 1,4-addition to the furan ring; hence, (IIa) and(IIb) are geometric isomers.

Thus the entire course of conversions of the products of the oxidation of the 2,5-dimethoxy-2,5-dihydrofurfuryl benzoates by performic acid can be represented by the scheme



Hence, the double bond of the isomeric benzoates (IIa) and (IIb) is not affected even on oxidation with per-formic acid.

Turning to the question of the stereochemistry of the methoxylated products (IIa) and (IIb), we shall examine very briefly the question of the methoxylation reaction mechanism, which, so far as we know, has not been considered previously. If it is assumed that the addition of bromine to the furan system goes by a two-step mechanism, as is the case in other electrophilic additions of bromine to unsaturated systems (see, for example, [14]), and that the addition leads preferentially to trans substitutuion, then the reaction mechanism of the furan ring methoxylation can be represented by the following general scheme:



The electrophilic attack of the bromine cation, directed toward the more nucleophilic carbon atom (in our case this is C_2), gives the cation (IX), which is subjected to further attack from the direction either of the bromine anion or a solvent anion (in our case the alkoxyl ion); in the first case the trans dibromide (Xa) is formed, and in the second, the trans alkoxybromide (Xb). The subsequent interaction of (Xa) and (Xb) with methanol in the presence of ammonia under the methoxylation reaction conditions goes in the first case with a double inversion of configuration and gives the trans-dimethoxy derivative (XIa), but in the second case with an inversion of configuration at only one carbon atom, forming the cis-isomer (XIb).

It is clear that under otherwise similar conditions the ratio (Xa): (Xb) depends on the concentration of the competing anions (bromine anion and alkoxyl anion), i.e., on the bromine concentration. Thus, when the bromine concentration is increased, the reaction should be directed toward (Xa) and (XIa); i.e., the quantity of the trans-isomer should increase. Indeed, an increase in the bromine concentration during the methoxylation reaction leads to an increase in the quantity of the solid isomer (IIa) and a decrease in the liquid isomer (IIb). Hence, it follows that the solid isomer must correspond to the trans-configuration (XIa), and the liquid isomer to the cis-configuration (XIb); this conclusion is also fully confirmed by a comparison of the melting points of the two isomers.

The material cited herein shows that the double bond in the 2,5-dimethoxy-2,5-dihydrofurfuryl benzoates is not affected even on oxidation by such a powerful epoxylating agent as performic acid. In the present case the action of the oxidant is directed at the lone hydrogen on C_3, after which the ring is opened, forming a keto-acid. A certain analogy to such an unusual course of the oxidation may be found in one of the works of Boeseken [15], who obtained derivatives of a butenolide on oxidizing furfuryl alcohol with per-acids.

The stability of the multiple bond (unusual in itself) in a derivative of dimethoxydihydrofurfuryl alcohol is unexpected enough, since analogous derivatives of furan are subject to oxidation, even though with considerable difficulty [16]. An explanation of the stability of the multiple bond in our case must in all probability be sought, apart from the strong electronegative effect of the oxygen atoms occurring in the vicinity of the double bond, also in the strong steric hindrances arising from the presence of the bulky benzoyloxy group, shielding both of the unsaturated carbon atoms.

EXPERIMENTAL

2,5-Dimethoxy-2,5-dihydrofurfuryl Benzoates

A 3-necked flask fitted with stirrer, dropping funnel, calcium chloride tube, and thermometer was charged with 72 g furfuryl benzoate in 100 ml anhydrous methanol; after cooling to −25°, a solution of 16.5 ml (0.36 mole) bromine in 100 ml anhydrous methanol was added, keeping the temperature below −20°. The mixture was stirred 1 hr at this temperature after adding the bromine, then cooled to −40°; cooling was then discontinued, and dry ammonia was passed through until a neutral reaction with universal indicator was obtained. Then the mixture was

stirred about 1 hr at room temperature, and the methanol was evaporated under vacuum. The dry residue was extracted with ether, the ether residue was filtered, and the ether was removed. The precipitated crystals of trans-2,5-dimethoxy-2,5-dihydrofurfuryl benzoate were filtered off, washed with alcohol, and dried. Yield 57 g (60.6%), m.p. 76-77° (from alcohol).

Found %: C 63.73, 63.79; H 6.07, 6.11. $C_{14}H_{16}O_5$. Calculated %: C 63.63; H 6.06.

The cis-isomer of 2,5-dimethoxy-2,5-dihydrofurfuryl benzoate was recovered by vacuum distillation of the remaining oil. Yield 19 g (20.4%).

B.p. 152-153° (2.5 mm), 125° (bath) ($6 \cdot 10^{-3}$ mm), n_D^{20} 1.5133, d_4^{20} 1.1770.
Found %: C 63.86, 63.89; H 6.15, 6.09. $C_{14}H_{16}O_5$. Calculated %: C 63.63; H 6.06.

On conducting the methoxylation under the same conditions, using higher bromine concentrations, the yield of the solid isomer increased.

trans-2,5-Dimethoxytetrahydrofurfuryl Benzoate. A 6.6-g quantity of the trans-isomer of 2,5-dimethoxydihydrofurfuryl benzoate was hydrogenated in ether on palladinized carbon for 3 days, until hydrogen absorption ceased. The solution was filtered, the ether was removed, and the residue was vacuum distilled. Yield of trans-2,5-dimethoxytetrahydrofurfuryl benzoate 5 g (75%).

B.p. 158° (3 mm), n_D^{20} 1.5075, d_4^{20} 1.1813.
Found %: C 62.78, 62.61; H 7.07, 6.92. $C_{14}H_{18}O_5$. Calculated %: C 63.14; H 6.82.

Bis-2,4-dinitrophenylhydrazone of ω-Benzoyloxylevulinaldehyde. A solution of 0.5 g trans-2,5-dimethoxytetrahydrofurfuryl benzoate in 20 ml ethanol was added to 0.74 g 2,4-dinitrophenylhydrazine in 100 ml alcohol, containing several drops of sulfuric acid. The mixture was boiled, and the yellow, almost alcohol-insoluble crystals were filtered out, washed with water to negative test for sulfate ion, and crystallized from xylene. Yield of bis-2,4-dinitrophenylhydrazone of ω-benzoyloxylevulinaldehyde 0.83 g (87%), m.p. 186-188° (decomp.).

Found %: C 49.64, 49.46; H 3.50, 3.49; N 19.72, 19.75. $C_{24}H_{20}O_{10}N_8$. Calculated %: C 49.65; H 3.47; N 19.31.

Performic Acid Oxidation of Isomeric 2,5-Dimethoxy-2,5-dihydrofurfuryl Benzoates

Oxidation of trans-Isomer. 1) A solution of 10 g of the trans-isomer of 2,5-dimethoxy-2,5-dihydrofurfuryl benzoate in 75 ml of anhydrous formic acid was cooled to 0°, 10 ml of 25% hydrogen peroxide was added, and the reaction mixture was shaken and allowed to stand two weeks at −10°. The crystalline precipitate was filtered out, washed with anhydrous formic acid, and thoroughly dried under vacuum. Yield of trans-5-benzoyloxy-4-ketopentene-2-oic acid 6.8 g, m.p. 172° (from anhydrous formic acid).

Found %: C 61.57; 61.67; H 4.38, 4.53. $C_{12}H_{10}O_5$. Calculated %: C 61.96; H 4.27.

S-Benzylisothiuronium salt, m.p. 144-145° (from alcohol).

After recovering the trans-5-benzoyloxy-4-ketopentene-2-oic acid, the mother liquor was evaporated under vacuum, and from the remaining oil (in a refrigerator) the corresponding cis-isomer crystallized out, m.p. 101-103° (from 30% alcohol); yield 1.2 g.

2) A 15-g quantity of the trans-isomer of 2,5-dimethoxy-2,5-dihydrofurfuryl benzoate was dissolved in 100 ml anhydrous formic acid, and 10 ml (0.074 mole) of 25% hydrogen peroxide was added. The mixture was shaken and left at room temperature for two weeks. The solution was evaporated to half-volume, and the crystalline precipitate of the trans-isomer of 5-benzoyloxy-2-ketopentene-2-oic acid was filtered out. Yield 0.8 g, m.p. 172° (from anhydrous formic acid). The mother liquor after separation of the trans-isomer was vacuum-evaporated, and from the remaining oil (in a refrigerator) the cis-isomer of 5-benzoyloxy-4-ketopentene-2-oic acid crystallized out. Yield 10.8 g, m.p. 101-103° (from 30% alcohol).

Found %: C 61.60, 61.62; H 4.20, 4.15. $C_{12}H_{10}O_5$. Calculated %: C 61.96; H 4.27.

S-Benzylisothiuronium salt, m.p. 134-135° (from alcohol).

Oxidation of cis-Isomer. A 2.42-g quantity of the cis-isomer of 2,5-dimethoxy-2,5-dihydrofurfuryl benzoate was dissolved in 30 ml of 85% formic acid, and 3 ml of 25% hydrogen peroxide was added. The mixture was left at room temperature for one week, and then the solvent was removed. The residue (slightly yellowish crystals) was

crystallized from 30% alcohol, obtaining 1.8 g of the cis-isomer of 5-benzoyloxy-4-ketopentene-2-oic acid, m.p 101-103°, which on the basis of IR spectrum and mixed-sample test was identical with the acid obtained in the previous case.

Conversions of trans-Isomer of 5-Benzoyloxy-4-ketopentene-2-oic Acid

2,3-Dibromo-5-benzoyloxy-4-ketopentanoic Acid (VIIa) was obtained by 36-hr agitation of a suspension of 1 g of the trans-isomer of 5-benzoyloxy-4-ketopentene-2-oic acid in 15 ml anhydrous formic acid with an equimolar quantity of bromine. After diluting the reaction mixture with distilled water, the dibromide crystallized and was filtered off. Yield 1.6 g, m.p. 155-156° (decomp.) (from anhydrous formic acid).

Found %: C 36.28, 36.48; H 2.39, 2.54. $C_{12}H_{10}O_5Br_2$. Calculated %: C 36.55; H 2.54.

5-Benzoyloxy-4-ketopentanoic Acid was obtained by the hydrogenation of 1.5 g of the trans-isomer of 5-benzoyloxy-4-ketopentene-2-oic acid in ethanol on palladinized barium sulfate. Yield 1.45 g, m.p. 115.5-116.5° (from 50% alcohol).

Found %: C 60.98, 60.90; H 5.04, 4.97. $C_{12}H_{12}O_5$. Calculated %: C 61.02; H 5.08.

Benzoate of trans-3,6-Endomethylene-1,2,3,6-tetrahydrophthaloyl Carbinol was obtained from 1.76 g trans-5-benzoyloxy-4-ketopentene-2-oic acid and an equimolar quantity of cyclopentadiene, after 12 hr at 100°. Yield 2 g, m.p. 149-151° (from toluene).

Found %: C 68.28, 68.36; H 5.49, 5.55. $C_{17}H_{16}O_5$. Calculated %: C 68.00; H 5.37.

Conversions of cis-Isomer of 5-Benzoyloxy-4-ketopentene-2-oic Acid

2,3-Dibromo-5-benzoyloxy-4-ketopentanoic Acid (VIIb) was obtained by the interaction of a solution of 1 g of the cis-isomer of 5-benzoyloxy-4-ketopentene-2-oic acid in 10 ml anhydrous formic acid with an equimolar quantity of bromine. After diluting the reaction mixture with distilled water, the dibromide crystallized and was filtered off. Yield 1.3 g, m.p. 160.5-161° (decomp.) (from anhydrous formic acid).

Found %: C 36.47, 36.28; H 2.51, 2.39. $C_{12}H_{10}O_5Br_2$. Calculated %: C 36.55; H 2.54.

5-Benzoyloxy-4-ketopentanoic Acid was obtained by hydrogenating 1.5 g of the cis-isomer of 5-benzoyloxy-4-ketopentene-2-oic acid in ethanol on palladinized barium sulfate. Yield 1.48 g, m.p. 115-116.5° (from 50% alcohol). A mixture of this substance with the sample obtained by hydrogenating the trans-isomer of 5-benzoyloxy-4-ketopentene-2-oic acid did not give any melting point depression.

Benzoate of cis-3,6-Endomethylene-1,2,3,6-tetrahydrophthaloyl Carbinol was obtained from 1.1 g cis-5-benzoyloxy-4-ketopentene-2-oic acid and an equimolar quantity of cyclopentadiene in alcohol after 12 hr at 100°. Yield 1.2 g, m.p. 128-129° (from alcohol). A mixed sample with the benzoate of trans-3,6-endomethylene-1,2,3,6-tetrahydrophthaloyl carbinol melted at 116-120°.

Found %: C 67.94, 68.08; H 5.58, 5.66. $C_{17}H_{16}O_5$. Calculated %: C 68.00; H 5.37.

SUMMARY

1. In the methoxylation of furfuryl benzoate by the action of bromine in methanol in the presence of ammonia, the two stereoisomeric 2,5-dimethoxy-2,5-dihydrofurfuryl benzoates have been obtained.

2. It has been shown that the double bond in the 2,5-dimethoxy-2,5-dihydrofurfuryl benzoates is distinguished by greater inertness with respect to hydroxylating agents.

3. It has been shown that the oxidation of the 2,5-dimethoxy-2,5-dihydrofurfuryl benzoates by performic acid results in the formation of cis-and trans-5-benzoyloxy-4-ketopentene-2-oic acids.

4. Observations have been made on the mechanism of the methoxylation reaction.

LITERATURE CITED

1. Brit. patent 595, 041; Chem. Abstracts 42, 2992 (1948).
2. U. S. patent 2,475,097; Chem. Abstracts 43, 7970 (1949).

3. H. Yoshiteru, J. Chem. Soc. Japan Pure Chem. Sec. 79, 1528 (1958); RZhKhim. 1960, No. 1, 1197.
4. Murakami, Séno, Khata, J. Chem. Soc. Japan Pure Chem. Sec. 77, 1040 (1956); RZhKhim. 1958, No. 1, 1281.
5. N. Clauson-Kaas, F. Limborg, Acta Chem. Scand. 6, 551 (1952).
6. I. Falkstop, D. Raleight, L. Schniepp, J. Am. Chem. Soc. 72, 869 (1950).
7. A. Marley, R. Raphael, J. Chem. Soc. 1958, 2625.
8. N. Clauson-Kaas, F. Limborg, Acta Chem. Scand. 1, 619 (1947).
9. R. Criegee, P. Dimroth, Ber. 90, 1070 (1957).
10. R. Woodward, F. Brutcher, J. Am. Chem. Soc. 80, 209 (1958).
11. H. Brunel, Chem. revs. 135, 1055 (1902).
12. K. Pandya, I. Thorpe, J. Chem. Soc. 123, 2852 (1923).
13. A. Cornilot, C. r. 179, 274 (1924).
14. A. Transis, J. Am. Chem. Soc. 47, 2340 (1925).
15. V. Boeseken, M. Bunge, Rec. trav. chim. 50, 1023 (1931).
16. N. Tormod, N. Elming, N. Clauson-Kaas, Acta Chem. Scand. 12, 53 (1958).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE MECHANISM OF THE REACTION OF CYANAMIDE WITH MONOBASIC FATTY ACIDS

A. E. Kretov and A. P. Momsenko

Dnepropetrovsk Institute of Chemical Technology
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3916-3921, December, 1961
Original article submitted September 22, 1960

The literature contains descriptions of the reactions of cyanamide with alcohols, phenols, oxides, thiophenols, organomagnesium compounds, and other substances [1-6]; there is practically no information on the reactions of cyanamide with aliphatic acids.

It is indicated in the literature [7] that anhydrous formic acid reacts with cyanamide, forming urea and carbon monoxide. Lactic and salicylic acids react only in the presence of alcohol. Urea and the ethyl ester of salicylic acid were isolated successfully from the reaction medium; the ester of lactic acid was not isolated. The role of the alcohol, which can react directly with cyanamide, was not ascertained. In the acylation of the sodium salt of cyanamide by anhydrides of fatty acids [8] the principal reaction products are acyl derivatives of cyanamide of the type RCONHCN and $(RCO)_2NCN$. These same compounds were obtained [5] in the interaction of acetyl chloride with cyanamide. However, they were not recovered in the pure form. These studies had only an exploratory character.

In a systematic study of the reactions of cyanamide with anhydrous aliphatic acids, we found that in the case of anhydrous formic acid the reaction goes (in contrast to the other acids of this series) exclusively toward the formation of the monoureide.

$$2HCOOH + H_2NCN \rightarrow H_2NCONH_2 + 2CO + H_2O$$
$$H_2NCONH_2 + HCOOH \rightarrow H_2NCONHCHO + H_2O$$

Subsequent members of the homologous series of aliphatic acids form both amides of the acids and also monoureides. As the molecular weight of the acids increases, the yield of ureides decreases, with a simultaneous increase in the yield of amides. The decrease in the yield of the acyl derivatives is explained by the fact that for the first members of the homologous series of acids the major quantity of the acyl derivatives is formed by the interaction of the anhydrides of the acids with urea. It is well known that the reaction rate of anhydrides with urea decreases as the molecular weight of the anhydrides increases [11-13]. Indeed, for higher aliphatic acids such as lauric, palmitic, and stearic, no ureides were obtained, and the yield of amides approached the theoretical. The absence of ureides is further explained by the fact that the urea which is formed as an intermediate product at high temperature with carboxylic acids gives amides, and the ureides decompose at this temperature; further, the urea itself decomposes at high temperatures into ammonia, carbonic acid, and cyanic acid, which is polymerized to cyanuric acid.

The correctness of our position is demonstrated by conducting the reaction of an anhydride with urea at a relatively low temperature, up to 120-130°; the ureide is formed. As the reaction temperature increases, a copious evolution of carbon dioxide begins, and the ureide yield decreases.

The reaction of cyanamide with substituted acids is of considerable interest [14-17]. Since the strongest action should be shown by substituents with a negative inductive effect in the α-position to the carboxyl group, the compounds used in the experiments were mono-, di-, and trichloroacetic, α-chloropropionic, and phenylacetic acids. The reaction, in contrast to the unsubstituted acids, was conducted both under mild conditions (not above 100° in benzene or dioxane solution) and under more severe conditions (at 125-135° in o-xylene solution, and at 155° in the case of phenylacetic acid).

If the reaction of cyanamide with the indicated acids is conducted under mild conditions, monochloroacetic acid forms both the amide and the monoureide, dichloroacetic the amide and only traces of the monoureide, phenylacetic the amide, and trichloroacetic and α-chloropropionic the monoureides only.

When the reaction is conducted under severe conditions, all of the acids give high yields of the amides.

On the basis of the obtained results, it may be assumed that for the substituted, as well as for the unsubstituted monobasic acids, the reaction proceeds by a single course; this allows the assumption of the following reaction mechanism:

$$2RCOOH + H_2NCN \rightarrow (RCO)_2O + H_2NCONH_2 \quad (1)$$

$$(RCO)_2O + H_2NCONH_2 \rightarrow RCONHCONH_2 + RCOOH \quad (2)$$

$$RCOOH + H_2NCONH_2 \rightarrow RCONH_2 + CO_2 + NH_3 \quad (3)$$

The following data can serve as confirmation of such a mechanism.

1. Cyanamide often behaves as a strong dehydrating agent [7]; the water that is formed in the reaction with acids interacts with the cyanamide, giving urea (Eq. 1).

Evidently another reaction course is also possible. Cyanamide and an acid form first an intermediate product, which then is converted to a monoureide, bypassing the stage of urea formation.

$$RCOOH + H_2NCN \rightarrow RCOOH \cdot NCNH_2 \rightarrow RCONHCONH_2 \quad (4)$$

And, finally, a third reaction course has been proposed by Dangyan [9, 10]:

$$RCOOH + H_2NCN \rightarrow RCOOH \cdot NCNH_2 \rightarrow RCONH_2 + HOCN \quad (5)$$

For evidence of the correctness of Eq. (1), a study was made of the reaction between cyanamide and anhydrous formic acid. If the starting materials are taken in equimolar quantities, the final product is urea, and only in the case of excess formic acid is the monoureide formed; in both cases carbon monoxide is evolved, since the anhydride of formic acid decomposes as soon as it is formed. If the reaction went according to Eq. (4), no carbon monoxide would be evolved, and with equimolar quantities of the reactants, the monoureide should be obtained. Equation (5) in general does not provide for obtaining both urea and the monoureide, and thus is inconsistent with the available experimental data. Thus, the data cited above confirm the correctness of Eq. (1) and the scheme that we have proposed.

On the other hand, the formation of anhydrides as intermediate substances is confirmed by the analogous reactions of carbodiimides with inorganic and organic acids [39-42]. Cyanamide in acidic medium also reacts in the carbodiimide form. The reaction that we studied (Eq. 1) is trimolecular, and therefore proceeds by a complex mechanism through a number of intermediate stages, most probably according to the scheme

$$H_2NCN \xrightarrow{H^+} HN{=}C{=}NH$$

$$HN{=}C{=}NH + H^+ \rightarrow \underset{(I)}{H_2\hat{N}{=}C{=}NH}$$

$$(I) + RCOO^- \rightarrow H_2NC(OOCR){=}NH$$

$$(II) + H^+ \rightarrow \underset{(II)}{H_2NC(OOCR){=}\hat{N}H_2}$$

$$(III) + RCOO^- \rightarrow \underset{(III)}{H_2NC(OOCR)(OOCR)NH_2} \rightarrow H_2NCONH_2 + (RCO)_2O$$

2. The intermediate compounds formed according to Eq. (1) – urea and the anhydride of the acid – interact, giving the monoureide. This reaction [11-13] was known long ago, and does not give rise to any doubt. However, monoureides were recovered only for low molecular weight or halogen-substituted acids. This is explained by the considerable dependence of the rate of reaction 2 on the activity of the anhydrides of the acids, which decreases with an increase in molecular weight of the latter; it is further explained by the decomposition of the monoureide at high temperature to an amide and cyanic acid. The latter is recovered in the form of the trimer [19].

$$3RCONHCONH_2 \rightarrow 3CH_3CONH_2 + C_3H_3O_3N_3 \quad (6)$$

As confirmation, the reaction of pelargonic acid with cyanamide was conducted at different temperatures. If the reaction is conducted at 130-140°, the amide of pelargonic acid, the monoureide, and a small quantity of cyanuric acid are obtained. At a higher temperature no monoureide was recovered; only the amide and cyanuric acid are obtained. For substituted acids the results are analogous.

Thus, the reaction represented by Eq. (2) is observed for all acids of the fatty series.

The third factor influencing the yield of monoureides of the higher acids is related to their capability of interacting with the acid according to the scheme

$$RCOOH + RCONHCONH_2 \rightarrow RCONH_2 + HOCONH_2 \quad (7)$$
$$\downarrow$$
$$CO_2 + NH_3$$

3. The reaction between urea and acids was known long ago [20-30]; however, the first detailed study of this reaction was conducted in 1946 [31]. The proposed reaction mechanism for obtaining an amide from urea and an acid is based on the interaction of the acid with urea with the formation of an intermediate compound (IV), which, either directly or with preliminary elimination of water, decomposes to the amide of the acid (V) and carbamino acid (VI), which is converted to carbon dioxide and ammonia.

$$RCOOH + H_2NCONH_2 \rightarrow \underset{\text{(IV)}}{RC(OH)(OH)-NHCONH_2} \rightarrow \underset{\text{(V)}}{RCONH_2} + \underset{\text{(VI)}}{HOCONH_2} \rightarrow CO_2 + NH_3$$

The detailed study of this reaction showed that acids of the fatty and fatty-aromatic series without additional functional groups can be converted smoothly to the corresponding amides, and dibasic acids give imides and diamides. The presence of additional functional groups in the acid (in the α- and β-positions) prevents the formation of amides [32-34].

It was shown [33-36] that the formation of amides from acids and urea goes by a complex mechanism. On heating, the urea decomposes to ammonia and cyanic acid (VII), which can polymerize partially to the trimer; the cyanic acid reacts with the carboxylic acid in the iso-form (VIII), forming an intermediate product which decomposes to the amide (V) and carbon dioxide.

$$H_2NCONH_2 \rightarrow NH_3 + \underset{\text{(VII)}}{NCOH}$$

$$\underset{\text{(VIII)}}{H-N=CO} + RCOOH \rightarrow H_2N-C(=O)-O-C(=O)-R \rightarrow \underset{\text{(V)}}{H_2NOCR} + CO_2$$

The results of our experiments agree with those described previously [33-36].

Mono- and dichloroacetic acids under mild conditions give a very low yield of the amide, and trichloroacetic and α-chloropropionic acids do not form any amides at all [18].

The increase in the yield of amides in the presence of cyanuric acid for halogen-substituted acids should be attributed principally to reactions 6 and 7. Acutally, not only for substituted acids, but also for the higher unsubstituted acids, when the reaction temperature was increased considerably, no ureides were obtained, there being recovered the amide, cyanuric acid, and the ammonium salt of the corresponding acid. In the case of low molecular weight acids, no cyanuric acid was recovered [37, 38].

EXPERIMENTAL

The reaction was conducted in a three-necked flask with a reflux condenser, dropping funnel, and thermometer; the top of the condenser was connected by an outlet tube to a Drexel [gas washing] bottle for collecting the carbon dioxide. The reaction flask with 0.74 mole of the acid was heated to 115°, and then 0.16 mole of cyanamide dissolved in 0.001* mole of the corresponding acid was added dropwise. In the case of butyric, isobutyric, and isovaleric acids the cyanamide was dissolved in 15 ml of dioxane. The end of the reaction was determined on the basis of the cessation of carbon dioxide evolution at the given temperature (120°). The precipitated monoureide was filtered out, and the filtrate was vacuum distilled to recover the amide. A brown undistilled residue remained in the bottom of the flask; this was washed with ether and alcohol. Judging by solubility and nitrogen content, this was a triazine derivative.

For the higher fatty acids, the reaction was conducted by an analogous method. It differed only in the temperature range of the reaction (140-210°) and the weights of the acids taken. In this case an excess of the acid is undesirable, since it hinders the purification of the final products.

The reaction with the halogen-substituted acids and the phenylacetic acid was conducted both under mild conditions, not above 100° (for phenylacetic acid 150° in solvent), and under severe conditions, at 125-135° in o-xylene (for pheylacetic acid at 180° without solvent).

The results of the experiments are presented in the table.

Acid	Content, %				Yield, %	
	N in amide		N in monoureide			
	found	calculated	found	calculated	Amide	Monoureide
Formic	-	-	31.4	31.8	-	100
Acetic	26.41	26.38	26.22	26.2	43.7	55.8
Propionic	19.1	19.15	24.9	24.9	62.0	31.9
Butyric	16.1	16.1	21.0	20.0	75.0	20.9
Isobutyric	16.08	16.07	-	-	71.6	-
Isovaleric	14.01	13.83	-	-	75.0	-
Enanthic [heptanoic]	10.6	10.0	-	-	77.4	-
Pelargonic	8.6	8.9	14.9	14.7	43.0	20.0
Lauric	7.04	7.02	-	-	86.0	-
Palmitic	5.6	5.48	-	-	86.7	-
Stearic	4.89	4.93	-	-	94.7	-
Monochloroacetic •	14.25	14.95	20.0	20.25	11.5	31.0
Monochloroacetic ••	14.13	14.95	20.0	20.25	75.0	-
Dichloroacetic •	10.0	10.93	-	traces	50.0	traces
Dichloroacetic ••	10.2	10.93	-	-	50.0	-
Trichloroacetic •	-	-	13.37	13.6	-	31.0
Trichloroacetic ••	8.92	8.61	-	-	72.0	-
Phenylacetic •	10.6	10.36	-	-	78.0	-
Phenylacetic •••	10.12	10.36	-	-	50.0	-
α-Chloropropionic •	-	-	18.0	18.6	-	27.7
α-Chloropropionic ••	12.9	13.02	-	-	25.0	-

•Reactions were conducted below 100°.

••Reaction temperature 125-135°.

•••Reaction temperature 180°.

SUMMARY

1. A study has been made of the reaction of cyanamide with low and higher molecular weight monobasic aliphatic acids, and also with α-halogen-substituted and phenylacetic acids.

*Quantity as in Russian original – Publisher.

2. A basis is given in stages for a proposed mechanism of the reaction of cyanamide with monobasic aliphatic acids.

3. A new method has been developed for preparing amides and monoureides of acids, which may find practical utilization.

LITERATURE CITED

1. H. Kolbe, J. pr. Ch. (2), 1, 288 (1870).
2. G. Meyer, J. pr. Ch. (2), 18, 419 (1878).
3. E. Drechsel, J. pr. Ch. (2), 21, 77 (1880).
4. P. Brigl, Ber. 45, 1557 (1912).
5. E. Drechsel, J. pr. Ch. (2), 11, 209, 284 (1875).
6. A. Hantzsch, E. F. Dollfus, Ber. 35, 256 (1902).
7. G. P. Seidler, J. pr. Ch. 21, (2), 129 (1880).
8. L. Martens, J. pr. Ch. (2), 17 1 (1878).
9. M. G. Dangyan, Izv. AN Arm. SSR, OKhN, No. 9-10, 23 (1942).
10. M. G. Dangyan, Izv. AN Arm. SSR, OKhN, No. 9-10, 23 (1942).
11. A. W. Hofmann, Ber. 14, 2733 (1881).
12. H. Arstfein, R. Bentley, J. Chem. Soc., 1951, 774, 3509.
13. Canadian patent 463,777 (1943).
14. R. Boivin, N. Briqo, J. Boivin, Arch. Pharm. 238/60, 139 (1955).
15. V. Tommasi, Bull. Soc. Chim. 19, 243 (1873).
16. L. Glermont, Am. Chim 2, (5), 420 (1874).
17. L. Glermont, R. Meldola, J. Am. Chem. Soc. 27, 404 (1874).
18. A. E. Kretov, A. P. Momsenko, ZhOKh 31, 2000 (1961).
19. Beilsf 3, 62 (1921).
20. E. Fischer, L. Poeder, Ber. 34, 3751 (1901).
21. H. Weidel, E. Poithner, Monatsh. 17, 182 (1896).
22. J. Horbaczewski, Monatsh. 8, 586 (1887).
23. H. Huppert, Ber. 6, 1278 (1873).
24. E. Grimaux, C. r. 83, 63 (1876).
25. A. Michal, Ann. Chem. J. 5, 198 (1883).
26. H. Biltz, Zieb. Ann. 368, 255 (1909).
27. A. W. Hofmann, Ber. 3, 771 (1870).
28. M. Nencki, Ber. 9, 235 (1876).
29. F. Wohler, Lieb. Ann. 62, 250 (1870).
30. A. Claus, O. Pentensen, J. pr. Ch. (2) 38, 208 (1888).
31. E. Cherbuleiz, Landolf, Helv. Chim. Acta. 29,1438 (1946).
32. J. Sikdar, T. W. Ghosh, J. India Chem. Soc. 25, 112 (1948).
33. A. Rahman, M. O. Farooq, Lieb. Ann. 585, 200 (1954).
34. A. Rahman, M. O. Farooq, C. r. 21, 338 (1952).
35. A. Rahman, Rec. trav. chim. 75, 2, 164 (1956).
36. A. Rahman, Zbl. 1957, 6645.
37. A. E. Kretov, A. P. Momsenko, Khimiya i khim. tekhnologiya 4, No. 1, 84 (1961).
38. A. E. Kretov, A. P. Momsenko. ZhOKh 31, 73 (1961).
39. H. G. Khorana, A. R. Todd, J. Chem. Soc. 1953, 2257.
40. H. G. Khorana, Chem. Revs. 53, 145 (1953).
41. J. G. Moffatt, H. G. Khorana, J. Am. Chem. Soc. 79, 33, 41 (1957).
42. M. Smith, J. G. Moffat, H. G. Khorana, J. Chem. Soc. 1958, 6204.

FURANIDINOPYRAZOLES

I. K. Korobitsyna, Yu. K. Yur'ev, Yin Ch'en-lieh,

A. F. Davydova, and N. N. Gaidamovich

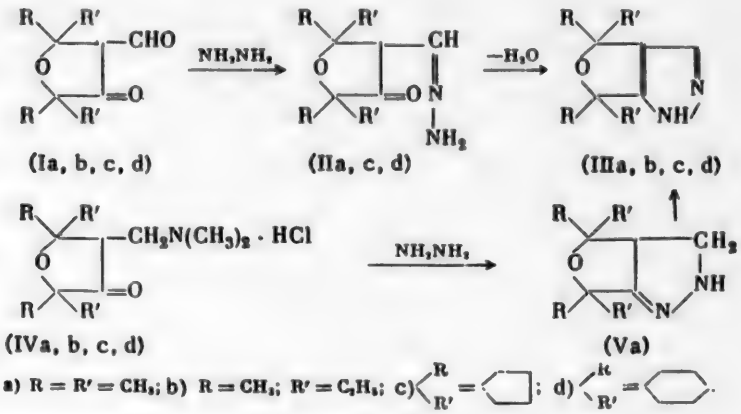
M. V. Lomonosov Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3921-3926, December, 1961
Original article submitted January 9, 1961

In the reaction of β-dicarbonyl compounds and hydrazine, the formation of pyrazoles proceeds simply, owing to the identity of positions 3 and 5 for pyrazoles that are not N-substituted [1, 2]. If the starting materials are an unsymmetrical β-dicarbonyl compound and a substituted hydrazine, either a mixture of isomeric pyrazoles or one of them is formed [3]. Another convenient method of synthesizing pyrazoles is dehydrogenation of the corresponding pyrazolines by sulfur [4]. A further advantage of this reaction is that, on obtaining N-substituted pyrazoles, their structure is strictly predetermined.

Continuing a study of the properties of our synthesized 4-oxymethylene- (I) and 4-dimethylaminomethyl-2,2-5,5-tetraalkylfuranidones-3 (IV) [5, 6], and having established that (I) gives a hydrazone (II) at the aldehyde group [7], we utilized these compounds for obtaining condensed systems containing a furanidine and a pyrazole ring.

In the present work we showed that the hydrazones (IIa, c, d) on vacuum distillation or heating above the melting point split out water, being converted to the corresponding 4,5-(3,4)-(2', 2',5',5'-tetraalkylfuranidino-3',4')-pyrazoles (IIIa, b, c, d). *



(Ia, b, c, d) (IIa, c, d) (IIIa, b, c, d)

(IVa, b, c, d) (Va)

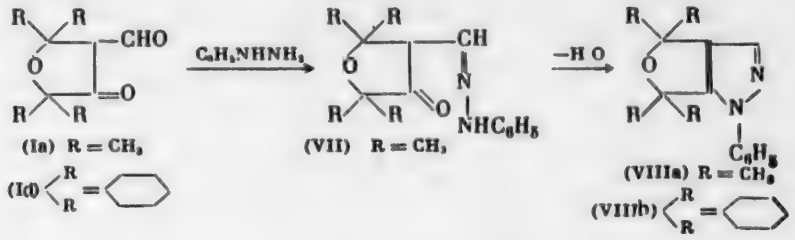
a) R = R′ = CH₃; b) R = CH₃; R′ = C₂H₅; c) R, R′ = ⬠; d) R, R′ = ⬡.

In the case of the furanidinopyrazole (IIIa) it was shown that it is a monomer and that it forms a benzoyl derivative (VI) (i.e., that it contains an NH group), and that its UV spectrum is analogous to the absorption spectrum of tetrahydroindazole (λ_{max} 220 mμ), which is characteristic for all homologs of pyrazole [8]. The IR spectrum gave an absorption band characteristic for the NH bond with a frequency of 3230 cm^{-1} (in the case of tetrahydroindazole the NH bond corresponds to a vibration with frequency 3190 cm^{-1}); corresponding to the conjugated double bond there are peaks in the region 1581 cm^{-1}.

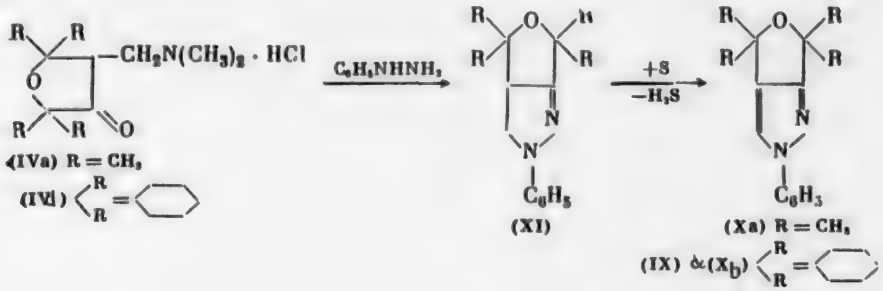
*In preparing the furanidinopyrazole (IIIb) the corresponding hydrazone was not isolated in pure form.

The furanidinopyrazoles (III) were also synthesized by another route – from the hydrochlorides of the corresponding Mannich bases (IV), which were converted by the action of hydrazine hydrate to the corresponding furanidinopyrazolines (V), of which only compound (Va) was isolated in the pure form, since the compounds were very readily oxidized in air. The dehydrogenation of the furnidinopyrazolines (V) by sulfur at 100-180° led to the furanidinopyrazoles (III). A comparison of these two methods of synthesis of the furanidinopyrazoles (III) shows that the first method gives better yields and is simpler.

We also established that the interaction of the oxymethylenefuranidone (Ia) with phenylhydrazine gives a phenylhydrazone (VII); since it is identical with the phyenylhydrazone obtained from 4-chloromethylene-2,2,5,5-tetramethylfuranidone-3, we consider that the reaction takes place at the aldehyde group. 1-Phenyl-4,5-(2',2',5',5'-tetramethylfuranidino-3',4')-pyrazole (VIIIa) was obtained on heating the phenylhydrazone (VII) with zinc chloride. 1-Phenyl-4,5-(2',2',5',5'-bispentamethylenefuranidino-3',4')-pyrazole (VIIIb) was obtained directly on heating the oxymethyleneketone (Id) with phenylhydrazine and sulfuric acid.



The interaction of the hydrochlorides of the Mannich bases (IVa) and (IVd) with phenylhydrazine and subsequent dehydrogenation of the resulting 1-phenyl-3,4-(2',2',5',5'-tetraalkylfuranidino-3',4')-pyrazolines (IX) with sulfur leads to the 1-phenyl-3,4-(2',2',5',5'-tetraalkylfuranidino-3',4')-pyrazoles (Xa, b).



Thus, 2,2,5,5-tetraalkylfuranidones-3 in the form of their 4-oxymethylene and 4-dimethylaminomethyl derivatives (I and IV, respectively) can serve as convenient starting materials for the synthesis of the isomeric 1-phenyl-4,5- (VIII) and 1-phenyl-3,4-(2',2',5',5'-tetraalkylfuranidino-3',4')-pyrazoles (X).

EXPERIMENTAL

4,5-(3,4)-(2',2',5',5'-Tetraalkylfuranidino-3',4')-pyrazoles (IIIa, b, c, d). a) To a solution of 0.02 mole of 4-oxymethylene-2,2,5,5-tetraalkylfuranidone-3 (Ia, c, d) in 30 ml ether, 0.04 mole hydrazine hydrate was added with stirring, the mixture was heated 30 min, and the ether was distilled off; the hydrazones (IIa, c,d) were recrystallized from ether.

Furanidinopyrazole (IIIa). The hydrazone (IIa) was heated with a reflux condenser in an oil bath; at 110° the substance melted, and at 125° it again solidified.

Furanidinopyrazoles (IIIc, d). The hydrazones (IIc, d) were vacuum distilled at 1-2 mm, obtaining thick oils which soon crystallized.

Constants and yields of the compounds obtained are shown in the table.

Name and empirical formula	Melting point	Yield (%) by method		Found %			Calculated %		
		a	b	C	H	N	C	H	N
Hydrazone of 4-formyl-2,2,5,5-tetramethyl-furanidone-3. $C_9H_{16}O_2N_2$ (IIa)	110-111*	98.5	-	58.75 58.66	8.86 8.80	15.54 15.57	58.68	8.75	15.24
3,4-(2',2',5',5'-Tetramethyl-furanidino-3',4')-pyrazoline. $C_9H_{16}ON_2$ (Va)	76-79	-	79	-	-	16.65 16.54	-	-	16.60
3,4-(4,5)-2',2',5',5'-Tetra-methylfuranidino-3',4')-pyrazole. $C_9H_{14}ON_2$ (IIIa)*	222.5-223	96	47	64.88 64.75	8.58 8.51	16.61 16.55	65.02	8.51	16.85
1-Benzoyl-3,4-(2',2',5',5'-tetramethylfuranidino-3',4') pyrazole. $C_{16}H_{18}O_2N_2$ (VI)	99-100	87**	-	70.73 70.82	6.83 6.69	10.29 10.24	71.08	6.71	10.36
3,4-(4,5)2',5'-Dimethyl-2',5'-diethylfuranidino-3',4'-pyrazole. $C_{11}H_{18}ON_2$ (IIIb)	127-127.5	60	41	68.12 68.20	9.40 9.42	14.44 14.59	68.01	9.38	14.42
Hydrazone of 4-formyl-2,2,5,5-bistetramethyl-enefuranidone-3. $C_{13}H_{20}O_2N_2$ (IIc)	97.5-98	90	-	66.76 66.84	8.35 8.50	11.89 12.03	66.78	8.53	11.85
3,4-(4,5)-2',2',5',5'-Bistetramethylene-furanidino-3',4')-pyrazole. $C_{13}H_{18}ON_2$ (IIIc)	152-153	50	52	71.46 71.63	8.25 8.34	13.09 13.17	71.53	8.31	12.85
Hydrazone of 4-formyl-2,2,5,5-bispentamethyl-enefuranidone-3. $C_{15}H_{24}O_2N_2$ (IId)	108-109	93	-	-	-	10.79 10.68	-	-	10.60
3,4-(4,5)-(2',2',5',5'-Bispentamethylene-furanidino-3',4')-pyrazole. $C_{15}H_{22}ON_2$ (IIId)	208-210	61	48	73.91 73.88	9.22 9.32	11.26 11.28	73.13	9.00	11.37

*M 171.1; calcd. 166.65.

**Compound (VI) was obtained by Schotten-Baumann benzoylation of compound (IIIa); recrystallized from aqueous alcohol.

Furanidinopyrazole (IIIb). A solution of 0.028 mole of the oxymethylenefuranidone (Ib) and 0.056 mole hydrazine hydrate in 30 ml ether was boiled while stirring for 30 min, the ether was evaporated, and the residue was vacuum distilled at 1-2 mm, obtaining a thick oil which soon crystallized.

The furanidinopyrazoles (IIIa, b, c, d) were recrystallized from petroleum ether.

b) To a solution of 0.066 mole hydrazine hydrate and 2 ml 40% NaOH solution in 15-20 ml alcohol, there was added over 20 min a solution of 0.022 mole of the Mannich base hydrochloride (IVa, b, c, d) in 20 ml alcohol; the mixture was boiled while stirring 3-4 hr, the alcohol was distilled off, the residue was extracted with ether, and the extract was dried with potassium carbonate. After distilling off the ether, the furanidinopyrazoline (V) crystallized after prolonged standing. This was heated to 100-180°, and 0.022 g-atom of sulfur was added at such a rate that the height of the hydrogen sulfide flame burning at the outlet of the Claisen flask did not exceed 1.5-2 cm. Then the solid mass was dissolved in absolute ether, the sulfur was filtered out, a stream of dry hydrogen chloride was passed into the solution, and the precipitated furanidinopyrazole hydrochlorides were separated, dissolved in 2 N sodium hydroxide, and extracted with ether. The extracts were dried with potassium carbonate, the ether was distilled off, and the furanidinopyrazoles (IIIa, b, c, d) crystallized.

Phenylhydrazone of 4-Oxymethylene-2,2,5,5-tetramethylfuranidone-3 (VII). a) To a solution of 0.02 mole of the oxymethylenefuranidone (Ia) in 30 ml ether, 0.02 mole phenylhydrazine was added while stirring; the mixture was heated 30 min, the ether was distilled off under vacuum, and the residue was washed with petroleum ether. M.p. 137-138° (from aqueous alcohol). Yield 68%.

Found %: N 11.15, 11.05. $C_{15}H_{20}O_2N_2$. Calculated %: N 10.77.

b) To 0.01 mole 4-chloromethylene-2,2,5,5-tetramethylfuranidone-3 in 30 ml ether, 0.01 mole phenylhydrazine was added while stirring; having removed the precipitate, the ether was distilled off under vacuum, and the residue was crystallized from aqueous alcohol. M. p. 137-138°, yield 76%. A mixed sample with the previous preparation did not show any melting point depression.

1-Phenyl-4,5-(2',2',5',5'-tetramethylfuranidino-3',4')-pyrazole (VIIIa). A 0.0015-mole quantity of the phenylhydrazone (VII) was heated 5 min at 150° with 0.4 g zinc chloride; the hot melt was pulverized and washed with water. M. p. 74.5-75.5° (from aqueous alcohol). Yield 65%.

Found %: C 74.76, 74.60; H 7.67, 7.74; N 11.57, 11.62. $C_{15}H_{18}ON_2$. Calculated %: C 74.38; H 7.45; N 11.56.

The phenylfuranidinopyrazole (VIIIa) was also obtained on heating equimolar quantities of the oxymethylenefuranidone (Ia) and phenylhydrazine with a small quantity of concentrated sulfuric acid.

1-Phenyl-4,5-(2',2',5',5'-bispentamethylenefuranidino-3',4')-pyrazole (VIIIb). A mixture of 0.006 mole of the oxymethylenefuranidone (Id), 0.006 mole phenylhydrazine, 0.3 g concentrated sulfuric acid, 2 ml water, and 20 ml alcohol was boiled 6 hr with stirring, made alkaline with 2 N sodium hydroxide solution, and extracted with ether. The extract was dried with anhydrous sodium sulfate, and the ether was distilled off. M. p. 109-110° (from alcohol). Yield 40%.

Found %: C 78.29, 78.52; H 8.35, 8.46; N 8.78, 8.72. $C_{21}H_{26}ON_2$. Calculated %: C 78.25; H 8.10; N 8.69.

1-Phenyl-3,4-(2',2',5',5'-tetramethylfuranidino-3',4')-pyrazole (Xa). A solution of 0.025 mole of the Mannich base hydrochloride (IVa) in 25 ml alcohol was added while stirring to a mixture of 0.027 mole phenylhydrazine and 2.5 ml 40% sodium hydroxide solution. The mixture was heated 5 hr, the alcohol was distilled off, and the residue wad dehydrogenated with sulfur as described above. Having dissolved the reaction product in methanol, the sulfur was separated off and the methanol was distilled off. M. p. 110.5-111° (from alcohol). Yield 57%.

Found %: C 74.84, 74.72; H 7.62, 7.50; N 11.59, 11.36. $C_{15}H_{18}ON_2$. Calculated %: C 74.38; H 7.45; N 11.56.

1-Phenyl-3,4-(2',2',5',5'-bispentamethylenefuranidino-3',4')-pyrazole (Xb). A solution of 0.01 mole of the Mannich base hydrochloride (IVd) in 30 ml alcohol was added while stirring to a mixture of 0.01 mole phenylhydrazine, 1 ml 40% sodium hydroxide solution and 15 ml alcohol. The mixture was boiled 15 hr, and the alcohol was distilled off under vacuum. Yield of the phenylfuranidinopyrazoline (IX) 50%. M. p. 127-128° (from aqueous acetone).

Found %: N 8.85, 8.80. $C_{21}H_{28}ON_2$. Calculated %: N 8.84.

A 0.0034-mole quantity of the phenylfuranidinopyrazoline (IX) was dehydrogenated with 0.0034 g-atom of sulfur at 200-250°. After treatment as described above, obtained the pehnylfuranidinopyrazole (Xb) with m.p. 92-93° (from alcohol); yield 70%.

Found %: C 77.68, 77.68; H 8.36, 8.20; N 8.36, 8.32. $C_{21}H_{26}ON_2$. Calculated %: C 78.25; H 8.10; N 8.69.

SUMMARY

1. 4,5-(3,4)-2',2',5',5'-Tetraalkylfuranidino-3',4')-pyrazoles have been prepared from 4-oxymethylene-2,2,5,5-tetraalkylfuranidones-3 and also from the hydrochlorides of 4-dimethylaminomethyl-2,2,5,5-tetraalkylfuranidones-3.

2. The method developed for the synthesis of isomeric 1-phenylfuranidinopyrazoles has made it possible to obtain: a) 1-phenyl-4,5-(2',2',5',5'-tetraalkylfuranidino-3',4')-pyrazoles from 4-oxymethylene-2,2,5,5-tetraalkylfuranidones-3; b) 1-phenyl-3,4-(2',2',5',5'-tetraalkylfuranidino-3',4')-pyrazoles from the hydrochlorides of 4-dimethylaminomethyl-2,2,5,5-tetraalkylfuranidones-3.

LITERATURE CITED

1. L. Knoor, Lieb. Ann. 279, 188 (1894); B. Sjollema, Lieb. Ann. 279, 248 (1894); L. Claisen, Lieb. Ann. 278, 261 (1893).
2. H. Henecka, Chemie der β-Dicarbonylverbindungen. Berlin, 332 (1950).
3. K. Auwers, Ch. Mansolf, Ber. 60, 1730 (1927).
4. I. I. Grandberg, A. N. Kost, ZhOKh 28, 3071 (1958); 29, 658 (1959); 30, 208 (1960).
5. I. K. Korobitsyna, T. A. Severina, Yu. K. Yur'ev, ZhOKh 29, 1960 (1959).
6. I. K. Korobitsyna, Yin Ch 'ên-lieh, Yu. K. Yur'ev, ZhOKh 30, 2214 (1960); 31, 2548 (1961).
7. I. K. Korobitsyna, I. I. Popova, N. N. Gaidamovich, Yu. K Yur'ev, ZhOKh 31, 2542 (1961).
8. P. Dayton, C. r. 236, 2515 (1953); I. I. Grandberg, A. N. Kost, ZhOKh 29, 658 (1959).

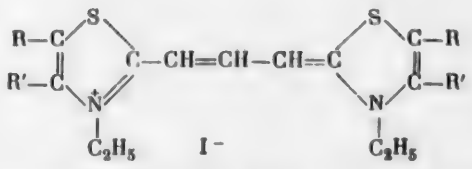
All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

STERIC HINDRANCE IN 4,4'-DIARYLTHIAZOLOCYANINE MOLECULES

E. D. Sych and A. I. Kiprianov

Institute of Organic Chemistry, Academy of Sciences, Ukr. SSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3926-3929, December, 1961
Original article submitted January 3, 1961

It is well known that the introduction of aryl radicals in place of hydrogen atoms at the 5,5' positions of the thiazolocarbocyanine molecule causes a strong shift of the absorption maximum of the dye toward the long-wave region. However, the introduction of the same substitutents in the 4,4' positions gives a much smaller change in the absorption maximum of the dye, and it is expecially noteworthy that various aryls give one and the same shift of the maximum. Absorption maxima are shown in the table for several dyes (in ethanol) of the general formula

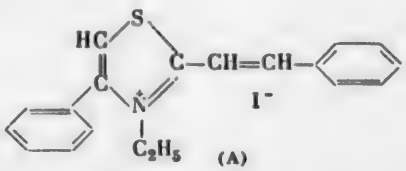


R	R'	Absorp. max (mμ)	Literature	R	R'	Absorp. max (mμ)	Literature
H	H	545	—	H	C_6H_5	—	—
C_6H_5	H	592	[1]	H	α-$C_{10}H_7$	560	[4]
α-$C_{10}H_7$	H	578	[2]	H	β-$C_{10}H_7$	560	[4]
β-$C_{10}H_7$	H	610	[3]	H	Benzofuryl-2	560	•
Benzofuryl-2	H	623	•				

•Our data.

Such a difference in effect on dye absorption of the same radicals in different positions of the thiazole ring may depend on the character of the conjugation of the aryl with the polymethine chromophore (in the 5,5' positions, conjugation through the nitrogen atoms, and in the 4,4' positions through the sulfur atoms). But there is also another cause that is extremely probable – the presence of spatial interference for 4, 4' aromatic substituents from the direction of the radicals at the nitrogen atoms. These interferences destroy the coplanarity and conjugation of the aryl with the thiazole ring. Theywere noted in an analogous case –for 4,4'-diaryloxazolocarbocyanines [5].

Using a method which one of us had propsoed previously [6], we were successful in proving experimentally the existence of steric hindrance in the molecule of 2-styryl-4-phenylthiazole ethiodide (A), which can be considered as a model of 4-arylthiazolocyanines.



(A)

In the absence of steric factors affecting light absorption, the absorption curve of a quaternary salt of a nitrogen heterocycle differs little from the absorption curve of its simple salt, for example, the sulfate. However, if the radical at the nitrogen atom hinders the coplanarity of the neighboring aryl with the heterocycle, the absorption curves of the simple and quaternary salts become markedly different: The absorption maximum of the quaternary salt is shifted toward the short-wave, and the band intensity decreases.

Just such a phenomenon is observed in the case of interest to us. Figure 1 shows absorption curves for 2-styryl-4-phenylthiazole in alcohol (I), its sulfate (solution of the base in a mixture of 4 volumes of alcohol and 6 volumes of concentrated sulfuric acid) (II), and its ethiodide in alcohol (III). It is found that the absorption band of the ethiodide (III) (λ_{max} 355 mμ, ε $1.82 \cdot 10^4$) is shifted considerably toward the short-wave region and is less intense than the absorption band of the sulfate of the same base (II) (λ_{max} 368 mμ, ε $2.4 \cdot 10^4$). •

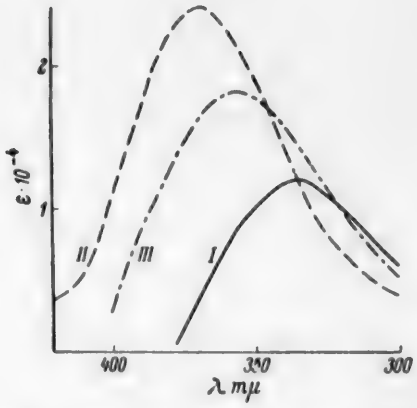


Fig. 1. Absorption curves of 2-styryl-4-phenylthiazole (I), its sulfate (II), and its ethiodide (III) in alcohol.

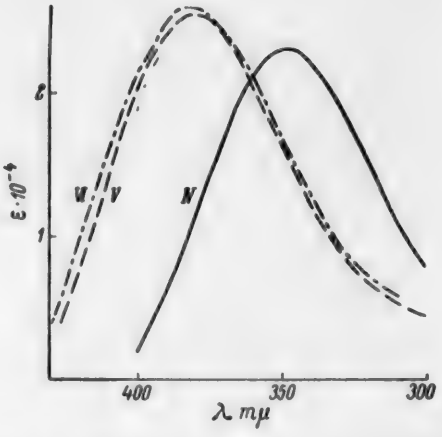


Fig. 2. Absorption curves of 2-styryl-5-phenylthiazole (IV), its sulfate (V), and its ethiodide (VI) in alcohol.

The absorption curves of 2-styryl-5-phenylthiazole (IV), its sulfate (V), and its ethiodide (VI) were determined under the same conditions. They are shown in Fig. 2.

As is evident from Fig. 2, in this case the absorption curves of the ethiodide and the sulfate coincide within the limits of experimental error, both as to position of the maximum (λ_{max} 380 mμ) and intensity (ε $2.6 \cdot 10^4$).

We used the absorption curves of 2-styryl-4-phenylthiazole and 2-styryl-5-phenylthiazole and of their sulfates to determine which of these two isomeric bases is the stronger. For this purpose, absorption curves were measured for both bases in a 1% alcoholic solution of sulfuric acid. A calculation carried out by the method of Firordt [7] showed that in 1% sulfuric acid the conversion to sulfate is about 10% for the 2-styryl-4-phenylthiazole and about 24% for the 2-styryl-5-phenylthiazole. Thus, the first base is considerably weaker, which, it is probable, is also determined to a certain degree by steric factors.

EXPERIMENTAL

2-Styryl-4-phenylthiazole is described in the literature [8]. We prepared it by a modified method. A mixture of 0.88 g 2-methyl-4-phenylthiazole, 0.5 g benzaldehyde, and 1 g fused zinc chloride was well mixed and heated 2.5 hr at 150-160° in a test tube with a calcium chloride tube. The reaction mass was treated with dilute (3:1) hydrochloric acid. The yellow-colored binary zinc salt which was recovered was decomposed by ammonia, and a benzene solution of the base was chromatographed on aluminum oxide. The fraction corresponding to 2-styryl-4-phenylthiazole was shaken with concentrated hydrochloric acid. The salt which was formed was filtered off, and

•It was established by separate experiments that the absorption curve of the ethiodide in alcohol coincides almost exactly with the curve of the ethiodide in alcoholic sulfuric acid solution of the indicated concentration.

the free base was liberated by a solution of ammonia. Colorless needles, m.p. 130° (from methanol) [8], λ_{max} 335mμ (in alcohol), ε $1.20 \cdot 10^4$.

2-Styryl-4-phenylthiazole Ethiodide. A mixture of 0.38 g of the ethyl-p-toluenesulfonate of 2-methyl-4-phenylthiazole and 0.1 g of benzaldehyde, in anhydrous alcohol with several drops of piperidine, was heated 40 min. The solution was diluted with water, treated with potassium iodide, and shaken with a mixture of benzene and ether. The viscous mass thus recovered solidified rapidly. The salt was recrystallized from water in the presence of bone char. Fine yellowish needles, m.p. 201°.

Found %: I 30.13, 30.07. $C_{19}H_{18}NSI$. Calculated %: I 30.29.

2-Styryl-5-phenylthiazole. A mixture of 7 g 2-methyl-5-phenylthiazole, 4.5 g benzaldehyde, and 3 g freshly fused zinc chloride was heated 13 hr at 130°. The yellow crystals were ground with dilute hydrochloric acid and benzene. The undissolved portion was the binary zinc salt of 2-styryl-5-phenylthiazole.

Found %: Cl 17.83, 18.00. $C_{17}H_{13}NS \cdot ZnCl_2$. Calcualted %: Cl 17.79.

The zinc salt of the styryl was shaken with 20% caustic. After extracting the mixture with benzene and evaporating the benzene extract, obtained 3.8 g (36%) of a compound in the form of yellowish prisms. M.p. 139° (from alcohol or petroleum ether). λ_{max} 347 mμ (in alcohol), ε $2.30 \cdot 10^4$.

Found %: N 5.46, 5.26; S 11.93, 11.85. $C_{17}H_{13}NS$. Calculated %: N 5.33; S 12.15.

2-Styryl-5-phenylthiazole Ethiodide. A mixture of 0.66 g of 2-methyl-5-phenylthiazole ethiodide and 0.2 g benzaldehyde in 3 ml anhydrous alcohol with 5 drops of piperidine was boiled 30 min. Precipitated a yellow crystalline sediment in amount 0.5 g (60%), m.p. 228° (from alcohol).

Found %: I 30.31, 29.94. $C_{19}H_{18}NSI$. Calculated %: I 30.31.

The spectra were measured on an SF-4 spectrophotometer.

SUMMARY

Absorption spectra have been measured for 2-styryl-4-phenylthiazole, 2-styryl-5-phenylthiazole, and their sulfates and ethiodides. It has been shown that the transition from the sulfate to the ethiodide for 2-styryl-4-phenylthiazole is accompanied by a considerable hypsochromic shift of the absorption maximum and a decrease of the extinction, whereas for 2-styryl-5-phenylthiazole the absorption curves of the sulfate and ethiodide almost coincide. Hence it follows that in the molecule of the 2-styryl-4-phenylthiazole ethiodide the phenyl group is not coplanar with the thiazole ring.

It has been shown that 2-styryl-5-phenylthiazole is a stronger base than 2-styryl-4-phenylthiazole.

LITERATURE CITED

1. B. S. Portnaya, I. I. Levkoev, N. S. Spasokukotskii, DAN SSSR 75, 231 (1950).
2. E. D. Sych, Ukr. khim. zh. 24, 90 (1958).
3. E. D. Sych, Ukr. khim. zh. 22, 217 (1956).
4. E. D. Sych, Ukr. khim. zh. 22, 80 (1956).
5. R. A. Jeffreys, J. Chem. Soc. 1952, 4823.
6. A. I. Kiprianov, V. A. Shrubovich, ZhOKh 26, 2891 (1956).
7. E. Stearns, Absorption Spectroscopy (Collection) IL, 289 (1953); A. I. Kiprianov, Yu. S. Rozum, ZhOKh 29, 1310 (1959).
8. W. H. Mills, J. Smith, J. Chem. Soc. 121, 1734 (1922).

S-DERIVATIVES OF THIOUREA

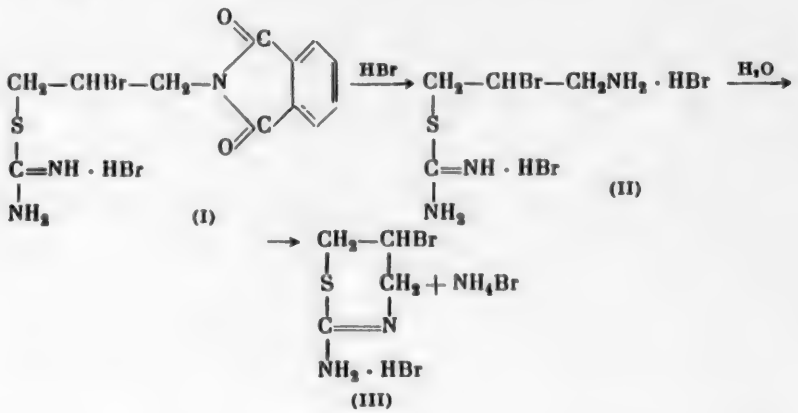
IV. PREPARATION OF 2-BROMO-3-ISOTHIURONIUMPROPYLAMINE AND STUDY OF SOME OF ITS TRANSFORMATIONS

V. M. Fedoseev, V. N. Bochkarev, and A. B. Silaev

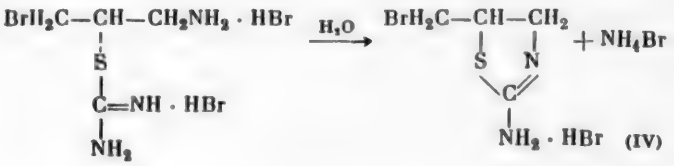
M. V. Lomonosov Moscow State University

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 3929-3933, December 1961
Original article submitted December 26, 1960

Previously we had shown [1] that the replacement of only one bromine atom occurs when N-(2,3-dibromopropyl)-phthalimide is reacted with thiourea, and the theory was expressed that the reaction product is N-[2-bromo-3-(isothiuronium bromide) propyl]-phthalimide (I). To confirm the validity of this formula, we studied in the given paper the properties of amine (II), obtained from the phthalimide after removal of the phthaloyl protection. It is known [2] that 2-aminoethylisothiuronium and 3-aminoproypylisothiuronium salts are smoothly cyclized in aqueous solutions to give 2-aminothiazoline and 2-aminopenthiazoline respectively. Consequently, in our case, if the proposed formula for phthalimide (I) is correct, then 2-amino-5-bromopenthiazoline (III) should be obtained as the result of the cyclization of the corresponding amine (II).



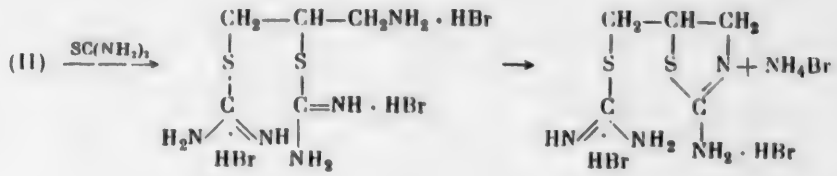
If the proposed formula is incorrect, and the bromine atom in the phthalimide molecule is located on the primary carbon atom, then 2-amino-5-bromomethylthiazoline (IV) should be formed when the corresponding amine is cyclized.



Following the course of all of the reactions was done by the paper chromatographic method, using a procedure similar to that described in [1], but employing the organic layer of the mixture n-butyl alcohol–12% hydrobromic acid (4:1) as the solvent in all of the experiments. The use of the acid completely prevented the cyclization of the amine during the chromatographing process.

It proved that the cyclization product of the amine had an R_f value of 0.63, and chromatographically was quite different from the hydrobromide of 2-amino-5-bromomethylthiazoline (R_f 0.74), synthesized previously by the method given in [3]. Isolation of the pure cyclization product, probably being the hydrobromide of 2-amino-5-bromopenthiazoline, proved impossible, since it during the isolation process, and also on further refluxing of the reaction solution, goes completely to the hydrobromide of 2-amino-5-bromo-methylthiazoline. It is probable that a conversion of the 6-membered penthiazoline ring to the more stable 5-membered thiazoline ring is observed in this case.

If the amine (II) obtained from (I) is reacted with thiourea, then, as was to be expected, 2-amino-5-isothiuroniummethylthiazoline is formed, which again testifies to the extreme instability of 2,3-diisothiuroniumpropylamine.



Chromatographic analysis revealed that it is the amine itself that reacts, and not its cyclization products.

To elucidate the quantitative relationships in the investigated reactions we synthesized 2-bromo-3-isothiuroniumpropylphthalimide, containing S^{35}, and investigated its transformations using the radiochromatographic method. The method of operation was described by us earlier [4]. It was found that the conversion of the starting phthalimide to the corresponding amine when the phthalimide is refluxed with concd. hydrobromic acid goes to the extent of 89% and is practically completed in one hour (Fig. 1).

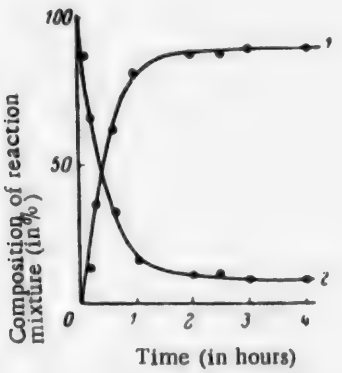


Fig. 1. Rate of formation of 2-bromo-3-(isothiuronium bromide)propylamine hydrobromide (1) when N-[2-bromo-3-(isothiuronium bromide)propyl]-phthalimide (2) is heated in refluxing 48% hydrobromic acid.

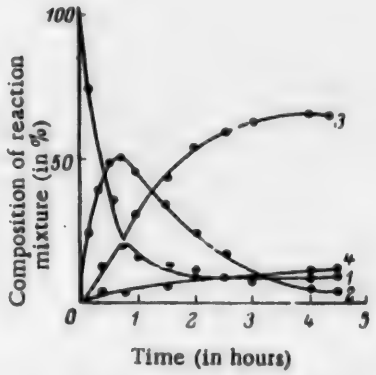


Fig. 2. Rate of cyclization of 2-bromo-3-(isothiuronium bromide)propylamine hydrobromide when refluxed in aqueous solution. 1) 2-Bromo-3-isothiuroniumpropylamine; 2) 2-amino-5-bromopenthiazoline (postulated primary cyclization product); 3) 2-amino-5-bromomethylthiazoline; 4) decomposition product of 2-amino-5-bromomethylthiazoline.

A study of the cyclization of the amine when its aqueous solution is refluxed revealed that conversion of the amine to the cyclic compound is practically complete in 1.5 hr, in which connection about 12% of the starting material remains in the mixture (Fig. 2, Curve 1).

The maximum yield (51%) of the primary cyclization product – the penthiazoline – is reached after 45 min (Fig. 2, Curve 2), while the greatest concentration of its transformation product – 2-amino-5-bromomethylthiazoline – is observed after 3 hr (Fig. 2, Curve 3). Curve 4 in Fig. 2 characterizes the formation rate of some unidentified substance, which, however, is not an intermediate cyclization product, since it is chromatographically identical (R_f 0.31) with the decomposition product of pure 2-amino-5-bromo-methylthiazoline when its aqueous solution is refluxed.

EXPERIMENTAL

Preparation of 2-bromo-3-(isothiuronium bromide)propylamine hydrobromide. A solution of 21.1 g of N-[2-bromo-3-(isothiuronium bromide)propyl]-phthalimide in 100 ml of 48% hydrobromic acid was refluxed for 2 hr. The obtained precipitate of phthalic acid was filtered, the mother liquor was evaporated in vacuo to dryness, and the residue was recrystallized from hydrobromic acid, followed by washing several times with anhydrous ether. We obtained 13.51 g (73%) of chromatographically pure substance (R_f 0.13). Colorless crystals with m.p. 187°. Readily soluble in water, methanol and ethanol, and insoluble in acetone and ether.

Found %: C 12.94, 12.92; H 2.99, 3.07; N 10.79, 11.00. $C_4H_{12}N_3SBr_3$. Calculated %: C12.83; H 3.23; N 11.25.

Dipicrate, m. p. 173 - 175° (from methanol).

Found %: C 28.64, 28.50; H 2.60, 2.59; N 18.62, 18.70. $C_{16}H_{16}O_{14}N_9SBr$. Calculated %: C 28.66; H 2.40; N 18.80.

Cyclization of 2-bromo-3-(isothiuronium bromide)propylamine hydrobromide. A solution of 1.91 g of the amine in 10 ml of water was refluxed for 8 hr. Chromatographic analysis revealed that after 30 min the solution contained the starting amine and a substance with R_f 0.63. After refluxing for 35 min a 3 ml aliquot of the reaction solution was taken and evaporated in vacuo to dryness. The residue was recrystallized from ethyl acetate and the obtained substance on chromatographing was found to have R_f 0.74 and contained only traces of the substance with R_f 0.63. Consequently, after refluxing for 8 hr, the entire solution was evaporated to dryness, and the obtained substance was separated from ammonium bromide by extraction with hot ethyl acetate. The ethyl acetate on cooling deposited a white crystalline substance with m. p. 137°, which did not depress the melting point when mixed with the hydrobromide of 2-amino-5-bromomethylthiazoline and was not different from it chromatographically.

Preparation of 2-amino-5-[(isothiuronium bromide)methyl]-thiazoline. A mixture of 0.382 g of 2-bromo-3-(isothiuronium bromide)propylamine and 0.779 g of thiourea in a mixture of 8 ml of anhydrous butanol and 2 ml of anhydrous methanol was refluxed for 5 hr. Chromatographic analysis of the reaction mixture at various intervals revealed that the cyclization products of the amine with R_f 0.63 and 0.74 were absent, i.e., the amine reacted with the thiourea in the uncyclized state. The obtained precipitate was filtered and then treated with a boiling mixture of ethyl acetate and methanol (1:1). We obtained 0.196 g (54%) of a white crystalline substance with m.p. 238-239° (from ethyl acetate).* The melting point was not depressed when it was mixed with the substance obtained by other procedures [5, 6], and it was not different from it chromatographically (R_f 0.13).

Synthesis of S^{35}-labeled compounds and radiochromatographic analysis. N-[2-Bromo-3-(isothiuronium bromide) propyl]-phthalimide was obtained by refluxing 10.30 g of the dibromopropylphthalimide and 1.88 g of thiourea-S^{35}, specific activity 50 millicuries/g, in 30 ml of anhydrous isobutyl alcohol for 18 hr. We obtained 5.43 g (52%) of substance with a specific activity of 3.2×10^8 impulses/min/g.

2-Bromo-3-(isothiuronium bromide)propylamine hydrobromide was obtained by refluxing 5.30 g of the phthalimide with the indicated specific activity in 25 ml of 48% hydrobromic acid for 4 hr. The rate of the reaction is plotted in Fig. 1. The reaction mixture was worked up in the same manner as in the preparation of the inactive compound. We obtained 2.97 g (63%) of the amine with a specific activity of 3.1×10^8 impulses/min/g.

*The melting point given in previous papers for 2-amino-5-isothiuroniummethylthiazoline obtained by reacting thiourea with 2,3-dibromopropylamine and with 2-amino-5-bromomethylthiazoline is incorrect. Verification revealed that the substances obtained by the two methods melt in the range 237-239°.

A solution of 0.010 g of the active amine and 0.372 g of amine not containing S^{35} in 4 ml of water was refluxed for 4.5 hr. Samples were removed from the reaction mixture at periodic intervals, which were deposited on strips of chromatographic paper. The development, treatment and analysis of the radiochromatograms were carried out as described previously. The results obtained on the rate of cyclization of the amine are plotted in Fig. 2.

SUMMARY

1. The previously expressed theory that the reaction product of N-(2,3-dibromopropyl)-phthalimide with thiourea is N-[2-bromo-3-(isothiuroniumbromide)propyl]-phthalimide was confirmed.

2. The hydrobromide of 2-bromo-3-(isothiuronium bromide)-propylamine was synthesized. Both the phthalimide and the amine, labeled with radioactive S^{35}, were prepared.

3. The method of paper radiochromatography was used to study the cyclization rate of the amine in water solution. It was postulated that the primary cyclization product is 2-amino-5-bromopenthiazoline.

LITERATURE CITED

1. V. M. Fedoseev, V. N. Bochkarev, A. B. Silaev, Zhur. Obshchei Khim. 30, 3795 (1960).
2. J. X. Khym, D. G. Doherty, R. Shapira, J. Am. Chem. Soc. 80, 3342 (1958).
3. A. E. Dixon, J. Chem. Soc. 69, 19 (1896).
4. V. M. Fedoseev, V. V. Ivanenkov, V. N. Bochkarev, Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol. 3, 484 (1960).
5. V. M. Fedoseev, S. P. Kovalenko, A. B. Silaev, A. N. Nesmeyanov, Zhur. Obshchei Khim. 29, 1703 (1959).
6. V. M. Fedoseev, V. V. Ivanenkov, A. B. Silaev, Zhur. Obshchei Khim. 30, 3468 (1960).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SYNTHESES OF SECONDARY AMINES OF THE THIOPHENE SERIES

B. P. Fedorov, G. I. Gorushkina, and Ya. L. Gol'dfarb

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3933-3939, December, 1961
Original article submitted January 6, 1961

In order to obtain some thiophene derivatives containing the dithiocarbamoyl grouping, $=N-CS-S-$, the need arose to prepare some secondary amines of structure RCH_2-NHR', where R is either the unsubstituted or substituted thiophene ring, while R' is either an alkyl group or also the thiophene ring.

Most of the secondary amines of the thiophene series described in the literature were obtained by reacting 2-thienyl-ω-haloalkanes, in particular 2-thenyl chloride, with primary amines [1-4]. The indicated method is not suitable for preparative purposes because the secondary amines are obtained in poor yields and are contaminated with large amounts of tertiary amines, and also for the reason that the synthesis of 2-thenyl halides goes in low yields (about 40%); in addition, compounds of this type are quite unstable. In one of our communications [5] we were also able to state that the reaction of 2-thenyl chloride with aromatic amines in the presence of potassium carbonate or pyridine gives the secondary amines in a yield of only 11-50%.

In this paper we give the results of our experiments on the preparation of secondary amines by the reduction of the corresponding azomethines. Here it should be mentioned that the aldehydes needed for the synthesis of the latter are readily available and are obtained in comparatively good yields. The azomethines were prepared from equimolecular amounts of the aldehyde and primary amine by the procedures: a) refluxing in benzene with a simultaneous removal of part of the benzene and the formed water by distillation; b) heating for 20-30 min in alcohol solution; and c) simple mixing of the aldehyde and amine (without solvent) under cooling. The azomethines prepared by one of these procedures are characterized in Table 1.

A large number of reagents [6] has been proposed for the reduction of azomethines to secondary amines. However, some of them, like Raney nickel, cannot be used on azomethines containing the thiophene ring because of reductive desulfurization. The action of the other reducing agents on such azomethines is not discussed in the literature. We collected some information on the problem in the course of the present investigation. The reduction of azomethines of the thiophene series with magnesium in methyl alcohol solution [7] gives the secondary amines in very low yields. Activated magnesium (like for the Grignard reaction) has been used [8] to obtain furfurylarylamines in 31-64% yield by the reduction of the corresponding azomethines. In our experiments the reduction under these conditions of azomethines containing the thiophene ring gave the corresponding secondary amines in 15-36% yield.

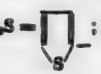
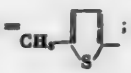
According to the literature data [9], the reduction of azomethines containing aromatic rings with aluminum lithium hydride in diethyl ether medium gives good yields (50-80%) of the secondary amines. The results of our experiments on the reduction of azomethines of the thiophene series with $LiAlH_4$ are in agreement with this information, and we were able to obtain the corresponding amines in yields as high as 70%. Nevertheless, it is impossible to consider this method as being suitable for preparative purposes, since it is linked with the peculiarities inherent to aluminum lithium hydride, such as sensitivity to moisture, fire hazard, tendency to explode in the dry state, etc.

As was shown on several examples of reducing azomethines [10, 11] prepared from aromatic aldehydes and amines, to the corresponding secondary amines, the above indicated disadvantages are eliminated completely by using either sodium or potassium borohydride in anhydrous methyl alcohol as the reducing agent. This method was successfully used by us to reduce the thiophene azomethines. Sodium borohydride reacts with methyl alcohol even at room temperature, liberating four molecules of hydrogen per molecule of compound [12]

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2$$

TABLE 1. RCH = NR'

Expt. No.	R	R'	B.p. (pressure in mm)	n_D^{20}	Method of preparation	Yield %	Empirical formula	Calculated %				Found %			
								C	H	N	S	C	H	N	S
I	C_4H_3S •	C_2H_5	90—92° (13)	1.5630	(b)	78.6	C_7H_9NS	60.41	6.55	—	22.98	60.78	6.42	—	22.32
II	2-CH_3—C_4H_2S•	C_2H_5	113—114 (18)	1.5640	(b)	66.0	$C_8H_{11}NS$	62.74	7.18	—	20.91	62.60	7.04	—	20.80
III	C_4H_3S	$CH_2CH(CH_3)_2$	110—112 (14)	1.5448	(c)	66.0	$C_9H_{13}NS$	—	—	8.38	—	—	—	8.04	—
IV	C_4H_3S	$CH_2CH_2CH(CH_3)_2$	133—134 (18)	1.5398	(b)	85.0	$C_{10}H_{15}NS$	66.29	8.28	—	17.67	66.33	8.50	—	17.47
V	2-CH_3—C_4H_2S	$CH_2CH_2CH(CH_3)_2$	145—146 (18)	1.5372	(b)	75.0	$C_{11}H_{17}NS$	67.69	8.71	—	16.41	67.48	8.83	—	16.26
VI	2-CH_3—C_4H_2S	$CH_2CH_2CH_2OH$	137—139 (1.5)	1.5825	(c)	52.6	$C_9H_{13}ONS$	59.0	7.10	—	17.84	58.74	7.26	—	17.34
VII	C_4H_3S	$CH_2C_4H_3S$	M.p. 55-56° (from methyl alcohol [13]	—	(a)	92.0	$C_{10}H_9NS_2$	57.96	4.34	—	30.93	57.92	4.52	—	30.73
VIII	C_4H_3S	$CH_2CH_2CH_2OH$	124—126 (1)	1.5860	(c)	60.0	$C_8H_{11}ONS$	56.72	6.55	—	18.94	56.98	6.41	—	18.61
IX	C_4H_3O•	$CH_2C_4H_3S$	M.p. 46—48 (from hexane)	—	(c)	86.7	$C_{10}H_9ONS$	62.79	4.75	—	16.71	63.0	4.48	—	16.66

• C_4H_3S =  ; 2-CH_3—C_4H_2S =  ; C_4H_3O = .

and apparently reducing the azomethine to the secondary amine in accordance with the scheme

$$RCH{=}NR' \xrightarrow[CH_3OH]{NaBH_4} RCH_2NHR'$$

which makes it possible to assume that theoretically 0.25 g-mole of $NaBH_4$ is sufficient to reduce one g-mole of the compound. However, as our experiments revealed, the reaction does not go to completion when this ratio of the reagents is used. In order to establish the most favorable ratio of the reagents in the reaction of our azomethines with sodium borohydride, we ran several experiments on the reduction of 2-thenylideneisoamylamine at 15-23°, taking 1, 0.75, 0.50 and 0.25 g-mole of reducing agent per g-mole of the base. In all cases except the last, the yield of the twice-distilled secondary amine was 75-80%. The yield of the secondary amine dropped to 40% when we used 0.25 g-mole of $NaBH_4$ per g-mole of the base. The secondary amines obtained by this procedure are characterized in Table 2, while in Table 3 we have listed the N-substituted thioureas* prepared from these amines by reaction with phenyl isothiocyanate.

EXPERIMENTAL

2-Thenylidene-2'-thenylamine (VII; method "a") was obtained from 12 g of 2-thenylamine and 11.88 g of 2-thiophenecarboxaldehyde in 80 ml of benzene, with standing of the reaction mixture overnight at room temperature. The liberated water (1.7 ml) was removed in a Dean–Stark apparatus, after which the benzene was distilled off under a slight vacuum. The residual oil crystallized. We obtained 20.4 g (92%) of substance with m. p. 55-56° (from methyl alcohol).

2-Thenylideneisoamylamine (IV; method "b") was obtained by mixing solutions of 17.2 g of isoamylamine in 30 ml of alcohol and 22.4 g of 2-thiophenecarboxaldehyde in 25 ml of alcohol, with stirring at room temperature. Here the temperature rose to 37°. After stirring for an hour, the mixture was allowed to stand overnight. The oil obtained on dilution of the reaction mixture with water (300 ml) was extracted with ether, and the ether solution was washed with water and then dried over magnesium sulfate. The oil remaining after removal of the ether by distillation was vacuum-distilled; here we collected 30.2 g (85%) of a fraction with b.p. 133-134° (18 mm) and n_D^{20} 1.5398.

Azomethines (I), (II) and (V) were obtained by the same procedure.

2-Furfurylidene-2'-thenylamine (IX; method "c") was obtained from 5.8 g of 2-thenylamine and 4.9 g of 2-furaldehyde, by stirring under ice-water cooling (temperature of the reaction medium was 5-8°). After stirring for 1 hour, the temperature of the reaction mixture was allowed to rise spontaneously to 30°. The obtained solid product was dissolved in ether, the liberated water was separated, and the ether solution was dried over magnesium sulfate. Removal of the ether by distillation left 8.58 g (86.7%) of substance; m.p. 46-48° (from hexane).

Azomethines (III), (VI) and (VIII) were also prepared by this procedure.

2-Thenylisoamylamine (XIIIa). With stirring, 4.47 g of pulverized 95% $NaBH_4$ was added in small portions to a solution of 18.9 g of 2-thenylideneisoamylamine (IV) in 120 ml of anhydrous methyl alcohol, cooled in ice to 3°, at such a rate that the temperature stayed in the range 15-22°. After stirring at this temperature for 30 min the mixture was poured into 200 ml of water. The obtained oil was extracted several times with ether, and the ether solution was washed with water and then dried over magnesium sulfate. The oil remaining after removal of the ether by distillation was distilled at 24 mm; here we collected 15.4 g (81.5%) of a fraction with b.p. 132-135° and n_D^{20} 1.5080. After redistillation, b.p. 132-133 (21 mm), n_D^{20} 1.5078.

The other reactant ratios used, and also the other secondary amines prepared by this procedure, are listed in Table 2.

N-Phenyl-N'-isoamyl-N'-(2-thenyl)thiourea (XXI) was obtained by shaking a mixture of 1.83 g of amine (XIII) and 1.41 g of phenyl isothiocyanate. Heat was developed and the solution quickly (3-5 min) thickened. On rubbing this solution a white precipitate began to form, which changed to a dense white mass. After rubbing with

*In all cases the found elemental analysis values are given as the average of two analyses.

TABLE 2. RCH_2NHR'

Expt. No.	R	R'	B.p.(pressure, mm)	n_D^{20}	d_4^{20}	A:$MeBH_4$*	Yield in%	Empirical formula	Calculated %				Found %			
									C	H	N	S	C	H	N	S
Xa	C_4H_3S	C_2H_5	79—80° (10)	1.5300	1.0264	1 : 1	84	$C_7H_{11}NS$	—	—	9.92	—	—	—	9.84	—
Xb	Same	Same	—	—	—	1 : 0.75	87	—	—	—	—	—	—	—	—	—
XI	$2\text{-}CH_3C_4H_2S$	C_2H_5	108 (18)	1.5210	1.0038	1 : 1.08	77	$C_8H_{13}NS$	61.89	8.59	—	20.65	61.70	8.46	—	20.44
XII	C_4H_3S	$CH_2CH(CH_3)_2$	112—113 (17)	1.5109	0.9848	1 : 1	76.5	$C_9H_{15}NS$	63.86	8.92	—	18.94	63.81	8.84	—	18.79
XIIIa	C_4H_3S	$CH_2CH_2CH(CH_3)_2$	132—133 (21)	1.5078	0.9734	1 : 1	81.5	$C_{10}H_{17}NS$	65.53	9.54	—	17.44	65.4	9.47	—	17.38
XIIIb	Same	Same	—	1.5083	—	1 : 0.75	93.0	—	—	—	—	—	—	—	—	—
XIIIc	Same	Same	—	1.5080	—	1 : 0.5	75.5	—	—	—	—	—	—	—	—	—
XIV	$2\text{-}CH_3C_4H_2S$	$CH_2CH_2CH(CH_3)_2$	147—147.5 (23)	1.5050	0.9575	1 : 1.2	67.1	$C_{11}H_{19}NS$	66.90	9.72	—	16.24	67.25	9.92	—	16.15
XV	$2\text{-}CH_3C_4H_2S$	$CH_2CH_2CH_2OH$	136—137 (1.6)	1.5452	1.1011	1 : 1	57	$C_9H_{15}ONS$	58.34	8.14	—	17.3	58.37	8.10	—	17.36
XVI	C_4H_3S	$CH_2C_4H_3S$	124—125 (1.5)	1.6062	1.2048	1 : 1	80.7	$C_{10}H_{11}NS_2$	57.38	5.30	—	30.62	57.57	5.53	—	30.48
XVII	C_4H_3O	$CH_2C_4H_3S$	115—116 (1.7)	1.5630	1.1625	1 : 0.75	75	$C_{10}H_{11}ONS$	62.14	5.74	—	16.59	61.87	5.91	—	16.41

*Molar ratios of azomethine (A) to $NaBH_4(KBH_4)$.

TABLE 3. N-Phenyl-N'-dialkylthioureas $\left(\begin{matrix}R'\\R\end{matrix}\!\!>\!N-CS-NH-C_6H_5\right)$

Expt. No.	R	R'	M.p.	Yield (in %)	Empirical formula	Calculated %			Found %		
						C	H	S	C	H	S
XVIII	$2\text{-}C_4H_3SCH_2$	C_2H_5	80—81° (a)	60.5	$C_{14}H_{16}N_2S_2$	60.84	5.83	23.20	60.98	5.92	22.88
XIX	$2,5\text{-}CH_3C_4H_2SCH_2$	C_2H_5	106—107 (a)	89	$C_{15}H_{18}N_2S_2$	62.05	6.23	22.07	62.05	6.27	22.04
XX	$2\text{-}C_4H_3SCH_2$	$CH_2CH(CH_3)_2$	92.5—94 (b)	~100	$C_{16}H_{20}N_2S_2$	63.20	6.65	21.05	63.33	6.75	20.86
XXI	$2\text{-}C_4H_3SCH_2$	$CH_2CH_2CH(CH_3)_2$	76—77 (a)	93	$C_{17}H_{22}N_2S_2$	64.11	6.99	20.12	64.32	7.20	19.60
XXII	$2,5\text{-}CH_3C_4H_2SCH_2$	$CH_3CH_2CH(CH_3)_2$	Thick viscous oil	86	$C_{18}H_{24}N_2S_2$	65.01	7.27	19.27	64.94	7.30	19.12
XXIII	$2,5\text{-}CH_3C_4H_2SCH_2$	$CH_2CH_2CH_2OH$	104—106 (c)	~100	$C_{16}H_{20}ON_2S_2$	59.96	6.30	20.0	60.12	6.22	19.86
XXIV	$2\text{-}C_4H_3SCH_2$	$2\text{-}C_4H_3SCH_2$	119—120 (d)	~100	$C_{17}H_{16}N_2S_3$	59.27	4.67	27.92	59.41	4.72	27.70
XXV	$2\text{-}C_4H_3SCH_2$	$2\text{-}C_4H_3OCH_2$	110—111 (a)	93	$C_{17}H_{16}ON_2S_2$	62.0	4.92	19.50	61.89	4.81	19.36

a) From 96% alcohol.

b) First chromatographed from benzene solution on Al_2O_3 and then recrystallized from 90% alcohol.

c) After three consecutive recrystallizations: from 90% alcohol, benzene, and alcohol.

d) From benzene and then from alcohol; according to the literature [14], the di-2-thenylamine obtained by the aminomethylation of thiophene does not give a crystalline derivative with phenyl isothiocyanate.

hexane, the reaction product was transferred to a filter, and washed with hexane and then with 50% alcohol. We obtained 3 g (93%) of substance; m. p. 76-77° (from 85% alcohol).

N-Phenyl-N'-isoamyl-N'-(5-methyl-2-thenyl)thiourea (XXII) was obtained from 1.97 g of 5-methyl-2-thenylisoamylamine and 1.41 g of phenyl isothiocyanate by heating on the water bath for 0.5 hr. After treating the liquid mass with alcohol, followed by the addition of several drops of water, the product crystallized. We obtained 2.85 g (85%) of product with an ill-defined melting point. After recrystallization from alcohol, followed by drying in vacuo at 60-70°, we obtained (XXII) as a pale yellow oil that decomposed on distillation.

The other thiourea derivatives were prepared in a similar manner.

SUMMARY

A method was developed for the preparation of secondary amines of the thiophene series, consisting of the reduction of the corresponding azomethines with sodium borohydride in anhydrous methyl alcohol.

LITERATURE CITED

1. F. Blicke, J. Burcke, J. Burckhalter, J. Am. Chem. Soc. 64, 477 (1942); L. Kyrides, F. Meyer, F. Zienty, J. Harvey, L. Bannister, J. Am Chem. Soc. 72, 745 (1950); U. S. Patent 2,624,743 (1953); C. A. 47, 11254 (1953).
2. F. Leonard, V.V. Solmessen, I. Am. Chem. Soc. 70, 2064 (1948); Brit. Patent 673, 633 (1952); C.A. 47, 5454 (1953).
3. F. F. Blicke, F. Leonard, J. Am. Chem. Soc. 74, 5105 (1952); U. S. Patent 2,518,351; C. A. 45, 4034d (1951); U. S. Patent 2,584,278 (1952); C. A. 47, 615g (1953).
4. J. Clark, R. Clapp, J. Vaughn, Jr., L. Sutherland, R. Winterbottom, G. Anderson, J. Forsythe, J. Blodinger, S. Eberlin, J. English, J. Org. Chem. 14, 216 (1949); K. Campbell, J. Ackerman, B. Campbell, J. Am. Chem. Soc. 71, 2905 (1949).
5. L. G. Angert, Ya. L. Gol'dfarb, G. I. Gorushkina, A. I. Zenchenko, A. S. Kuz'minskii, B. P. Fedorov, Zhur. Priklad. Khim. 32, 408 (1959).
6. Houben-Weyl, Methoden der organischen Chemie XI, 618-671 (1957).
7. L. Zechmeister, J. Truka, Ber. 63, 2883 (1930).
8. V. Hahn, R. Hansal, I. Markovčič, D. Vargazon, Arhiv kem. 26, 21 (1954).
9. A. Sommers, S. Aaland, J. Org. Chem. 21, 484 (1956); J. Billman, K. Tai, J. Org. Chem. 23, 535 (1958); N. G. Gaylord, Reduction With Complex Metal Hydrides [Russian translation] (1959).
10. Z. Horii, T. Sakai, T. Inoi, J. Pharm. Soc. Japan 75, 1161 (1955).
11. J. Billman, A. Diesing, J. Org. Ch. 22, 1068 (1957).
12. H. Schlesingen, H. Brown, H. Hoekstra, L. Rapp, J. Am. Chem. Soc. 75, 199 (1953).
13. H. Hartough, J. Am. Chem. Soc. 69, 1355 (1947).
14. H. Hartough, S. Lukasiewicz, E. H. Murray, Jr., J. Am. Chem. Soc. 70, 1146 (1948).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

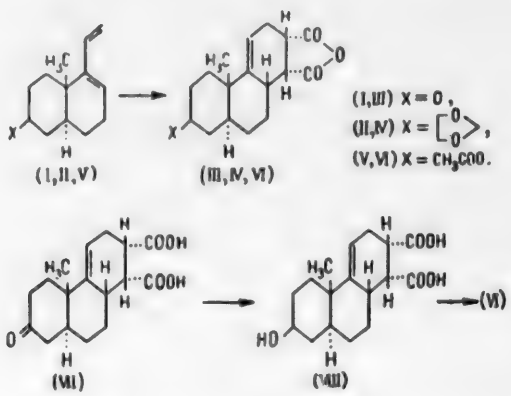
XLIII. STEREOCHEMISTRY OF THE DIENE CONDENSATION OF TRANS-1-VINYL-6-ACETOXY-9-METHYL-Δ^1-OCTAHYDRONAPHTHALENE WITH MALEIC ANHYDRIDE AND SOME TRANSFORMATIONS OF DICARBOXYLIC ACIDS OF THE DODECAHYDROPHENANTHRENE SERIES

I. A. Gurvich, I. M. Mil'shtein, and V. F. Kucherov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp 3939-3945, December, 1961
Original article submitted January 6, 1961

As had been shown in a previous communication [1], the condensation of trans-1-vinyl-6-oxo-9-methyl-Δ^1-octahydronaphthalene (I) and trans-1-vinyl-6-ethylenedioxy-9-methyl-Δ^1-octahydronaphthalene (II) with maleic anhydride leads to the predominant formation of adducts (III) and (IV), belonging to the same steric series. Earlier, on the example of the condensation of diene (I) and 1-vinyl-6-acetoxy-9-methyl-Δ^1-octahydronaphthalene (V) with benzoquinone [2], it was established that a similar stereospecific direction of the diene synthesis also occurs in these cases.

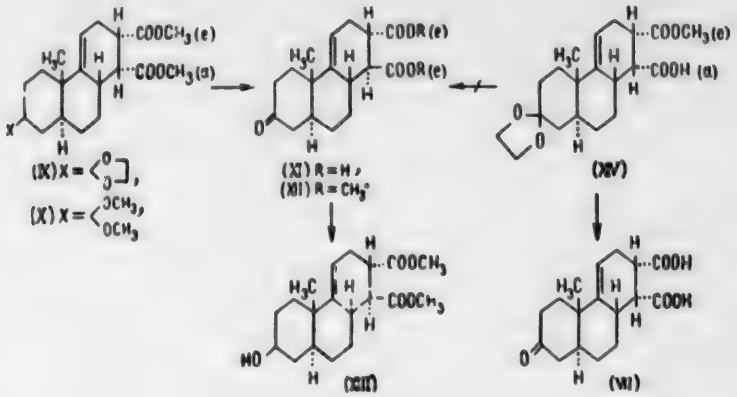
In the present paper we condensed diene (V) with maleic anhydride and were able to show that the main reaction product (VI) obtained here has the same configuration as adducts (III) and (IV).



The acid (VII) obtained from the hydrolysis of anhydride (III) was reduced with sodium borohydride to hydroxy acid (VIII), the acetylation of which with acetic anhydride in pyridine gave the acetoxy anhydride (VI), formed as the main isomer in the direct diene synthesis. As a result, it can be considered as proved that the sterospecific direction of the diene condensation with 6-substituted trans-1-vinyl-9-methyl-Δ^1-octahydronaphthalenes (I, II, V) is determined mainly by the angular methyl group present and depends but slightly on the character of the substituents attached to C_6.

It seemed of interest to study some of the stereochemical transformations of the dicarboxylic acids of the dodecahydrophenanthrene series obtained by us (alkaline isomerization of the carboxyl groups, isomerization of the double bond, etc.), which might supply additional proof for the configurations assigned to them. However, the use of compounds with unprotected keto group for these reactions seemed impractical. Consequently, we used the ketals of diesters (IX) and (X), obtained previously [1], to study the alkaline isomerization of the carbomethoxyl groups.

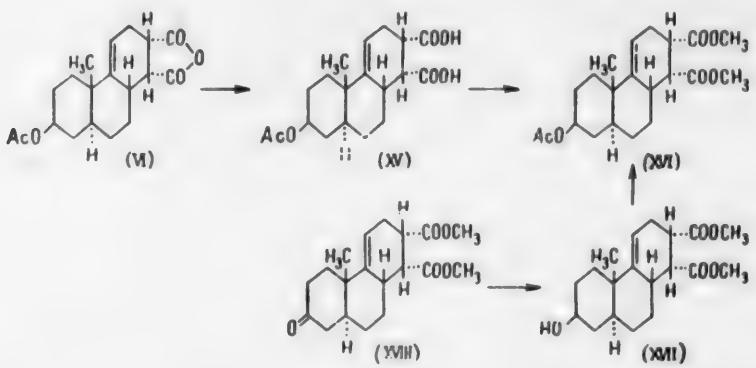
The isomerization of these esters with sodium methylate, followed by acidification of the reaction product, gave us the 7-keto-trans-dicarboxylic acid (XI), characterized as the diester (XII) corresponding to it, which, from the method of synthesis, should have a stable anti-trans configuration with a diequatorial arrangement of the carboxyl groups [3]. Reduction of trans-acid (XI) with sodium borohydride gave us the corresponding hydroxy acid, characterized as the diester (XIII).



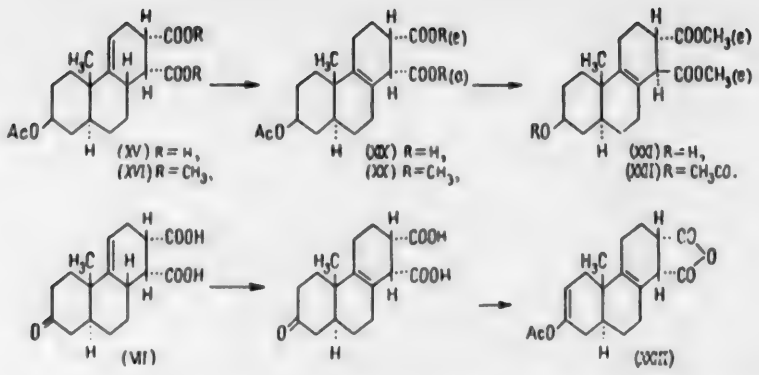
Only the starting cis-acid (VII) was isolated when we attempted to isomerize the previously obtained polyester ketal (XIV), for which the structure with the carbomethoxyl group attached to C_2 had been adopted [1], under the same conditions. This fact indicates that the carbomethoxyl group in polyester (XIV) occupies an equatorial position, and the cyclohexene ring in the polyester itself is incapable of conversion transformations [4].

To obtain compounds with a shifted double bond we utilized the 7-acetoxy derivatives of the cis-dicarboxylic acids, the snythesis of which was accomplished by the following scheme:

The hydrolysis of acetoxy anhydride (VI) gave acetoxy acid (XV), which when treated with diazomethane gave the corresponding diester (XVI). The latter can also be obtained by the acetylation of hydroxy diester (XVII), which in turn is formed by the reaction



of hydroxy acid (VIII) with diazomethane or by the reduction of keto diester (XVIII). When acetoxy acid (XV) was heated in acetic acid solution saturated with hydrogen chloride, we isolated a new dicarboxylic cis-acid (XIX), which was different from all of the previously described acids. This acid forms the corresponding diester (XX), which can also be obtained by the analogous acid isomerization of diester (XVI). The alkaline isomerization of diester (XX) easily gives the hydroxy trans-acid with an equatorial arrangement of the carboxyl groups, which was characterized as the hydroxy diester (XXI) and the acetoxy diester (XXII).



Since under acid isomerization conditions, which can lead either to a shift of the double bond or to the formation of the lactone [5], we obtained a new dicarboxylic acid (XIX), it is possible to assume that the latter has the double bond in the position between the rings, and consequently possible lactonization is absent here. An attempt to shift the double bond in acid (VII), containing an unprotected keto group, was accompanied by partial tarring, and when the reaction products were treated with acetic anhydride we were able to isolate only the enol acetate of the anhydride (XXIII) in the pure state. The latter proved to be different from the enol acetate obtained from anhydride (III), and this causes us to postulate that enol acetate (XXIII) has the double bond in the position between the rings.

EXPERIMENTAL

Condensation of acetate of trans-1-vinyl-6-hydroxy-9-methyl-Δ^1-octahydronaphthalene (V) with maleic anhydride. To obtain diene (V), a solution of 150 mg of lithium borohydride in 30 ml of ether was added, with stirring, to a solution of 0.9 g of crystalline diene (I) in 25 ml of absolute ether. The stirring was continued for 4 hr. Then 12 ml of 5% sulfuric acid was added, and after the usual treatment and drying of the ether solution we isolated 0.9 g of oil from it, which was treated with 1.5 ml of acetic anhydride and 1.5 ml of dry pyridine. The next day the experiment was worked up in customary manner. We obtained about 0.9 g of crude diene (V) as an oil, which was treated with a solution of 0.45 g of maleic anhydride in 4 ml of benzene. The condensation goes with considerable heat evolution. The mixture was allowed to stand overnight at room temperature. Then the benzene was distilled off, and treatment of the residue with ether caused the material to crystallize. We obtained 0.9 g of mixed adducts with m.p. 150-158°, from which by recrystallization from benzene we isolated 460 mg of acetoxy anhydride (VI) with m.p. 189-190°.

ν (in $CHCl_3$): 1851 cm^{-1} (K 536), 1778 cm^{-1} (K 2110), 1719 cm^{-1} (K 1180).
Found %: C 68.66, 68.44; H 7.21, 7.34. $C_{19}H_{24}O_5$. Calculated %: C 68.65; H 7.28.

We were unable to isolate any other pure products from the mother liquors.

Preparation of acetoxy anhydride (VI). A solution of 110 mg of NaOH in 3 ml of water and 50 ml of alcohol was added to 400 mg of keto acid (VII), and then with stirring and ice-water cooling, 50 mg of sodium borohydride was added gradually to the obtained soltuion. The reaction mass was stirred for 1.5 hr with ice-water cooling, and then for 2.5 at room temperature. The next day several drops of acetic acid were added and the solvent was distilled off in vacuo to dryness. Then the residue was treated with 20 ml of water and the obtained suspension was acidified to Congo with 5% sulfuric acid, after which the obtained precipitate was filtered and then recrystallized from aqueous methanol. We obtained 360 mg of hydroxy acid (VIII), which melted at 292-295°, with prior softening at 214-215°. A mixture of 140 mg of hydroxy acid (VIII), 1.4 ml of pyridine and 1 ml of acetic anhydride were vacuum-distilled, while the residual crystals were filtered and then washed in succession with ether, 1% sulfuric acid and water. We obtained 80 mg of acetoxy anhydride (VI) with m.p. 187-188°, which failed to depress the melting point when mixed with the specimen obtained above.

Trans-keto dicarboxylic acid (XI). a) To a solution of 2 g of sodium in 35 ml of anhydrous methnol was added 0.53 g of the ketal of cis-diester (IX) [1] and the mixture was heated under reflux for 15.5 hr. Then the methanol was distilled off, followed by the addition of water, which was distilled off on the boiling water bath under a slight vacuum. The addition of the water and its removal by distillation was repeated twice, after which the solution was

acidified with hydrochloric acid and the crystals obtained were filtered. We obtained 320 mg of trans-keto acid (XI) with m.p. 224-225° (from acetone), which after drying in vacuo had m. p. 231-232°.

Found %: C 66.69, 66.88; H 7.24, 7.32. $C_{17}H_{22}O_5$. Calculated %: C 66.65; H, 7.24.

b) Under analogous conditions, we obtained 3 g of acid (XI) from 4 g of the ketal of cis-diester (X) [1].

Diester of trans-keto dicarboxylic acid (XII). A solution of 0.1 g of acid (XI) in acetone was treated with an ether solution of diazomethane. The solvents were removed by vacuum-distillation and the residue was recrystallized first from hexane, and then from aqueous methanol. The obtained diester melted at 128-128.5°.

ν (in $CHCl_3$): 1728 cm^{-1} (K 2340), 1711 cm^{-1} (K 1890).
Found %: C 68.23, 68.14; H 7.76, 7.81. $C_{19}H_{26}O_5$. Calculated %: C 68.24; H 7.84.

The mixed melting point with cis-diester (XVIII) was 116-124°.

Trans-hydroxy diester (XIII). A solution of 140 mg of KOH in 5 ml of water and 60 ml of alcohol was added to 0.4 g of trans-keto acid (XI). Then, with stirring and water cooling, 60 mg of sodium borohydride was added in portions. The next day two drops of acetic acid were added and the solvents were distilled off in vacuo to dryness. The residue was treated with water and the obtained solution was acidified to give a precipitate. We filtered off 0.4 g of crude hydroxy acid with m.p. 243-244°, which was treated with an ether solution of diazomethane. After recrystallization from hexane and two recrystallizations from aqueous acetone we obtained the trans-hydroxy diester (XIII) with m. p. 135-136°.

ν (in $CHCl_3$): 1734 cm^{-1} (K 2050), 1033 cm^{-1} (K 204).
Found %: C 67.85, 67. 70; H 8.47, 8.49. $C_{19}H_{28}O_5$. Calculated %: C 67.83; H 8.39.

Attempted isomerization of polyester (XIV). To a solution of 2 g of sodium in 40 ml of methanol was added 0.6 g of polyester (XIV) [1] and the obtained solution was refluxed for 16 hr. The reaction product was worked up as described above. We obtained 0.32 g of keto acid (VII) with m.p. 192-194°, which after recrystallization from aqueous acetone melted at 198-199° and did not depress the melting point when mixed with the authentic specimen. The diester obtained from this acid melted at 131-132° and did not depress the melting point when mixed with the authentic diester (XVIII) [1].

Hydroxy diester (XVII). a) A suspension of 250 mg of hydroxy acid (VIII) in ether was treated with an ether solution of diazomethane. Then the solvent was distilled off to dryness and the residue was recrystallized first from hexane and then from aqueous methanol. We obtained 170 mg of hydroxy diester (XVII) with m.p. 69-70°.

Found %: C 67.61, 67.69; H 8.52, 8.44. $C_{19}H_{28}O_5$. Calculated %: C 67.83; H 8.39.

b) With stirring and ice-water cooling, a solution of 120 mg of lithium borohydride in 50 ml of ether was added in 1 hr to a suspension of 1.4 g of keto diester (XVIII) [1] in 50 ml of ether. The reaction mass was stirred for 3.5 hr with ice-water cooling, after which it was acidified with 5% sulfuric acid until acid to Congo. The ether layer was separated, washed with aqueous sodium bicarbonate solution and then with water, the solvent was vacuum-distilled, and the residue was recrystallized from aqueous methanol. We obtained 960 mg of hydroxy diester (XVII) with m.p. 68-69°, which proved to be identical with the specimen obtained above.

Acetate of hydroxy acid (XV). A solution of 120 mg of acetoxy anhydride (VI) in 5 ml of 80% aqueous dioxane solution was refluxed for 9 hr. After removal of the dioxane by distillation and recrystallization of the residue from aqueous methanol we obtained 90 mg of acetoxy acid (XV) with m.p. 214-215°.

Found %: C 65.17, 65.22; H 7.41, 7.47. $C_{19}H_{26}O_6$. Calculated %: C 65.12; H 7.48.

Acetate of hydroxy diester (XVI). a) A suspension of 70 mg of acetoxy acid (XV) in ether was treated with diazomethane and the solvent was vacuum-distilled. After recrystallization from hexane and two recrystallizations from aqueous methanol the acetoxy diester (XVI) melted at 103.5-104.5°.

ν (in $CHCl_3$): 1734 cm^{-1} (K 2930).
Found %: C 66.63, 66.67; H 7.90, 8.05. $C_{21}H_{30}O_6$. Calculated %: C 66.64; H 7.99.

b) A mixture of 340 mg of hydroxy diester (XVII), 3.4 ml of pyridine and 1.7 ml of acetic anhydride was allowed to stand overnight at room temperature. The next day the liquid products were vacuum-distilled and the

residue was extracted with benzene. The benzene solution was washed with 1% sulfuric acid, then with water, and dried over magnesium sulfate. The solvent was distilled off and the residue was recrystallized from aqueous methanol. We obtained 280 mg of the acetate of hydroxy diester (XVI) with m.p. 102.5-103°, which did not depress the melting point when mixed with the specimen obtained above.

Acetate of hydroxy acid (XIX). A solution of 700 mg of hydroxy acid acetate (XV) in 10 ml of glacial acetic acid saturated with hydrogen chloride was heated for 4 hr at 60-65°. The acetic acid was vacuum-distilled, after which the residue was treated with 20 ml of benzene and the solvent was removed by vacuum-distillation. This operation was repeated twice, after which the obtained residue was filtered and washed with ether. We obtained 600 mg of the hydroxy acid acetate (XIX) with m.p. 191-192° (from aqueous dioxane).

Found %: C 62.22, 61.94; H 7.67, 7.72. $C_{19}H_{28}O_8 \cdot H_2O$. Calculated %: C 61.94; H 7.66.

Acetate of hydroxy diester (XX). a) A suspension of 270 mg of hydroxy acid acetate (XIX) in ether was treated with an excess of diazomethane in ether solution, after which the solvent was removed by distillation and the residue was recrystallized first from hexane and then from aqueous methanol. We obtained 200 mg of the hydroxy diester acetate (XX) with m. p. 120-121.5°.

ν (in $CHCl_3$): 1734 cm^{-1} (K 2850).
Found %: C 66.38, 66.51; H 7.88, 7.94. $C_{21}H_{30}O_8$. Calculated %: C 66.64; H 7.99.

b) A solution of 280 mg of acetoxy diester (XVI) in 3 ml of glacial acetic acid saturated with HCl was heated for 4 hr at 50-60°, after which the acetic acid was vacuum-distilled and the residue was treated 3 times with benzene, with removal of the benzene by distillation after each treatment. After recrystallization of the residue from aqueous methanol we obtained 240 mg of acetoxy diester (XX) with m. p. 119-120°, which failed to depress the melting point when mixed with the above-described specimen.

Trans-hydroxy diester (XXI). To a solution of 3 g of sodium in 60 ml of anhydrous methanol was added 900 mg of acetoxy diester (XX), after which the solution was refluxed for 15 hr. Then the methanol was vacuum-distilled, after which water was added to the residue and then removed by distillation on the boiling water bath under a slight vacuum. Then the residue was dissolved in water and the solution was acidified with hydrochloric acid. The obtained crystals were filtered. We obtained 500 mg of the trans-hydroxy acid with m.p. 231-232° (from aqueous methanol). This acid (400 mg) was treated with an ether solution of diazomethane. After removal of the solvent by distillation and recrystallization of the residue from heptane we obtained 350 mg of the trans-hydroxy diester (XXI) with m.p. 132-133° (from aqueous methanol).

Found %: C 67.78, 67.82; H 8.39, 8.40. $C_{19}H_{28}O_8$. Calculated %: C 67.83; H 8.39.

Acetate of trans-hydroxy diester (XXII). A mixture of 150 mg of hydroxy diester (XXI), 1.5 ml of pyridine and 0.7 ml of acetic anhydride was allowed to stand overnight at room temperature. The next day the solvent was distilled off, while the residue was dissolved in benzene, and the benzene solution was washed first with 1% sulfuric acid and then with water. After drying, removal of the solvent by distillation, and recrystallization of the residue from aqueous methanol we isolated 120 mg of the trans-acetoxy diester (XXII), with m. p. 93-94°.

ν (in $CHCl_3$): 1736 cm^{-1} (K 2620).
Found %: C 66.45; H 7.96. $C_{21}H_{30}O_8$. Calculated %: C 66.64; H 7.99.

Enol acetate of the anhydride (XXIII). A mixture of 200 mg of keto acid (VII), 6 ml of dioxane and 3 ml of glacial acetic acid, the latter saturated with hydrogen chloride, was heated for 4 hr at 60-65°. The solvents were vacuum-distilled and the residue was worked up to give 150 mg of crude keto acid with m. p. 217-218° (from dioxane), which was refluxed for 8 hr in a mixture of 2 ml of acetyl chloride and 2 ml of acetic anhydride. After removal of the solvent by vacuum-distillation, the residue was evaporated 3 times in vacuo with benzene, and then recrystallized from a mixture of benzene and hexane. We obtained 120 mg of the anhydride enol acetate (XXIII) with m. p. 172-174° (from benzene).

Found %: C 68.78, 68.75; H 6.73, 6.67. $C_{19}H_{22}O_5$. Calculated: C 69.07; H 6.71.

The enol acetate of anhydride (III), obtained under analogous conditions, had m. p. 152-153°.

SUMMARY

1. A study was made of the diene condensation of trans-1-vinyl-6-acetoxy-9-methyl-Δ^1-octahydronaphthalene with maleic anhydride and it was shown that the steric direction of the diene synthesis involving 6-substituted trans-1-vinyl-9-methyl-Δ^1-octahydronaphthalenes is but slightly dependent on the character of the substituent attached to C_6.

2. A study was made of both the alkaline and acid isomerization of some derivatives of known dodechydrophenanthrenecarboxylic acids and the trans-dicarboxylic acid of this series, the acid with a shifted double bond, and a number of their derivatives, were prepared.

LITERATURE CITED

1. V. F. Kucherov, I. M. Mil'shtein, I. A. Gurvich, Zhur. Obshchei Khim. 31, 2832 (1961).
2. V. F. Kucherov, I. A. Gurvich, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1961, 1152.
3. I. N. Nazarov, V. F. Kucherov, V. M. Andreev, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1956, 817.
4. V. M. Andreev, L. K. Lysanchuk, V F. Kucherov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1960, 1084.
5. I. N. Nazarov, V. F. Kucherov, V. M. Andreev, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1956, 951.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

THE PREPARATION OF ALLENE

Ya. M. Slobodin and A. P. Khitrov

All-Union Scientific Research Institute of Petrochemical Processes
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3945-3947, December, 1961
Original article submitted February 6, 1961

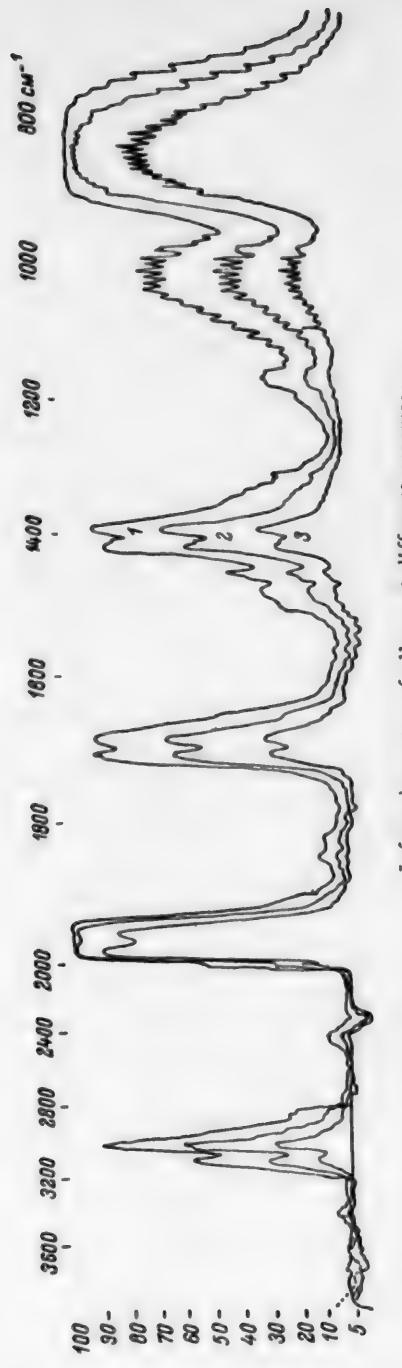
Allenic hydrocarbons occupy an important position among compounds that display a high tendency to polymerize. However, very few papers have been devoted to a study of the properties of allenes, chiefly because of the absence of convenient ways of preparing these hydrocarbons in a sufficiently pure state. Allene is usually prepared by the method developed by G. G. Gustavson [1], which consists of treating 2,3-dibromopropene with zinc dust in alcohol medium; in turn, the 2,3-dibromopropene is obtained by heating 1,2,3-tribromopropane with solid sodium hydroxide.

A serious disadvantage of the indicated method is the fact that the obtained allene contains a substantial amount of the volatile 2-bromopropene, representing the product of the side reduction of the starting dibromide. As was established by S. V. Lebedev [2], the presence of even traces of 2-bromopropene has a deleterious effect on the polymerization of allene, while the removal of this undesirable bromide impurity from the allene is fraught with great difficulties. Lebedev was unable to obtain a completely pure allene. That a certain amount of 2-bromopropene is present in the allene obtained by the indicated method was also shown by other authors [3], who, despite resort to specially built rectification apparatus, were also unable to obtain an allene that was completely free of the bromide impurity.

Values of the Main Absorption Frequencies in the Infrared Spectrum of Allene

From [5]		From [6]		Our data	
Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
852	very strong	852	very strong	850	very strong
1031	strong	1031	medium	1030	medium
1165	very weak	1165	very weak	1170	very weak
1389	strong	1389	strong	1387	strong
1684	medium	1700	medium	1700	strong
1956	very strong	1980	strong	1980	very strong
2420	weak	2420	weak	2400	very weak
2960	weak	2960	medium	2985	strong

In view of the practical importance of obtaining a pure allene, we investigated the possibility of using some other solvents for the reaction of 2,3-dibromopropene with zinc dust. It was established that the allene obtained in n-butyl alcohol medium also contains 2-bromopropene. As other solvents for the reaction we investigated diisopropyl ether, dioxane, acetonitrile, diethyl formal, butyl acetate, and isoamyl acetate. The reaction went sluggishly when diisopropyl ether, dioxane or acetonitrile was used, and the yield of allene was small. In the case of diethyl formal the reaction went slowly at the start, and then somewhat stormily with strong frothing. The best results were obtained using either butyl acetate or isoamyl acetate. In both solvents the reaction goes smoothly and quite rapidly. The allene obtained here contains neither 2-bromopropene nor methylacetylene. The yield of allene is nearly quantitative (95-98%). With all of the indicated solvents, the reaction was run under identical conditions, by the slow addition of 2,3-dibromopropene to a flask containing a vigorously stirred suspension of zinc dust in the investigated solvent, with heating on the boiling water bath. The 2,3-dibromopropene was prepared by the procedure given in [4].



Infrared spectra of allene at different pressures. 1) At 100 mm; 2) at 50 mm; 3) at 15 mm.

We took the infrared spectrum of the allene (figure) prepared in butyl acetate, in which connection the gas was not subjected to any prior purification. A Hilger H-800 infrared spectrometer was used to take the spectrum, at gas pressures of 100, 50, and 15 mm. The numerical values of the absorption frequencies when compared with the literature data are given in the table.

The absence of absorption in the 1600 cm^{-1} region, characteristic for the $CH_2 = CBr -$ group, testifies to the fact that the obtained allene does not contain 2-bromopropene in determinable amounts, while the excellent agreement of the frequency values and the absorption intensities with the literature data proves the high purity of the compound. A sample of the allene was polymerized, and the polymerizate gave a negative test for halogen, which confirmed the absence of bromide in the starting gas.

SUMMARY

1. It was shown that it is possible to use butyl acetate and isoamyl acetate as solvents in the preparation of allene by the Gustavson method. The yield of allene reaches 95-98%. Analysis of the infrared spectrum of the obtained allene established that both 2-bromopropene and methylacetylene were absent as impurities.

2. The reaction of 2,3-dibromopropene with zinc dust in butyl acetate medium can be recommended as a way of preparing pure allene.

LITERATURE CITED

1. G. G. Gustavson, Zhur. Russ. Fiz.-Khim. Obshchestva 20, 615 (1888).
2. S. V. Lebedev, Zhur. Russ. Fiz.-Khim. Obshchestva 45, 1249, (1913).
3. A. T. Blomquist, J. A. Verdol, J. Am. Chem. Soc. 78, 109 (1956).
4. Organic Syntheses [Russian translation] Coll. Vol. I, p. 191 (1949).
5. H. Kopper, A. Pongratz, Monatsh. 62, 78 (1933).
6. J. W. Linnett, W. H. Avery, J. Chem. Phys. 6, 686 (1938).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ORGANIC INSECTOFUNGICIDES

LXI. SYNTHESIS OF SOME MIXED ETHYLMERCAPTOETHYL THIOPHOSPHATES

Ya. A. Mandel'baum, N. N. Mel'nikov, Z. M. Bakanova, and P. G. Zaks

Ya. V. Samoilov Scientific Institute for Fertilizers and Insectofungicides (NIUIF), Moscow

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 3947-3949, December, 1961
Original article submitted January 5, 1961

It was recently shown in our laboratory that many mixed esters of thiophosphoric acid possess a high contact and systemic insecticidal activity and represent practical interest for use in agriculture [1-4]. In order to accumulate some information on the relationship between insecticidal activity and structure it seemed of interest to synthesize some mixed ethylmercaptoethyl thiophosphates, containing aliphatic and aromatic radicals, since thiophosphates of such structure are unknown in the literature.

Properties of O-Alkyl-O-aryl-O-2-ethylmercaptoethyl Thiophosphates of General Formula $\begin{matrix}\text{ArO}\\\text{RO}\end{matrix}\!\!>\!\text{P(S)OCH}_2\text{CH}_2\text{SC}_2\text{H}_5$

R	Ar	Yield (in %)	d_4^{20}	n_D^{20}	B.p. (pressure in mm)	Empirical formula	% P found	% P calculated
C_2H_5	C_6H_5	88	1.1910	1.5400	163-166° (0.5-0.6)	$C_{12}H_{19}O_3S_2P$	9.97,9.69	10.13
C_2H_5	$p\text{-}O_2NC_6H_4$	40	1.3282	1.5680	•	$C_{12}H_{18}O_5NS_2P$	9.46,9.53	8.83
C_2H_5	$p\text{-}ClC_6H_4$	80	1.2723	1.5510	•	$C_{12}H_{18}O_3S_2PCl$	9.08,9.18,11.0†• 10.80••	9.10,10.42••
CH_3	C_6H_5	50	1.2150	1.5540	•	$C_{11}H_{17}O_3S_2P$	10.33,10.56	10.64
CH_3	$p\text{-}O_2NC_6H_4$	40	1.3655	1.5880	•	$C_{11}H_{16}O_5NS_2P$	9.0,9.15	9.22
CH_3	$p\text{-}ClC_6H_4$	46	1.3548	1.5690	•	$C_{11}H_{16}O_3S_2PCl$	10.05,9.98	9.55

•Does not distill at 0.1-0.3 mm.
••Chlorine analysis.

Synthesis of the O-alkyl-O-aryl-O-ethylmercaptoethyl thiophosphates was accomplished by reacting the recently described [5, 6] alkyl aryl chlorothiophosphates with 2-hydroxyethyl ethyl sulfide in the presence of aqueous sodium hydroxide:

$$\begin{matrix}\text{ArO}\\\text{RO}\end{matrix}\!\!>\!\text{P(S)Cl} + \text{HOCH}_2\text{CH}_2\text{SC}_2\text{H}_5 + \text{NaOH} \rightarrow \begin{matrix}\text{ArO}\\\text{RO}\end{matrix}\!\!>\!\text{P(S)OCH}_2\text{CH}_2\text{SC}_2\text{H}_5 + \text{NaCl} + \text{H}_2\text{O}$$

The compounds synthesized in this manner are listed in the table. A study of the insecticidal properties of the synthesized compounds toward the rice weevil revealed that in their insecticidal action these compounds are

only slightly inferior to methylmercaptophos. The obtained compounds also possess the properties of systemic insecticides and acaricides. The LD_{50} of most of the compounds lies within 0.02-0.25%.

EXPERIMENTAL

All of the O-alkyl-O-aryl-O-2-ethylmercaptoethyl thiophosphates were synthesized under the following conditions. Aqueous NaOH solution (40%) was added gradually, with good stirring and cooling, to a mixture composed of equimolecular amounts of 2-hydroxyethyl ethyl sulfide and O-alkyl-O-aryl chlorothiophosphate. We took 1.5 g-mole of NaOH per g-mole of starting O-alkyl-O-aryl chlorothiophosphate. The temperature of the reaction mixture was held within 20-30°. When all of the NaOH solution had been added, the reaction mixture was kept an additional 1-3 hr at 20-30° with good stirring, after which it was diluted with water, and the oily layer was separated, washed with water, and dried over calcium chloride. The thus obtained product was then distilled in a high vacuum, while in the case of the compounds that could not be distilled in a high vacuum without decomposition, the light fractions were removed from them by vacuum-distillation.

The obtained compounds and their properties are given in the table.

SUMMARY

In order to accumulate some information on the relationship between the insecticidal activity of organic phosphorus compounds and their structure we synthesized a number of previously unknown O-alkyl-O-aryl-O-2-ethylmercaptoethyl thiophosphates. Some of the synthesized compounds are quite powerful insecticides.

LITERATURE CITED

1. N. N. Mel'nikov, Transactions of the First Conference on the Chemistry and Application of Organophosphorus Compounds [in Russian] Izd. AN SSSR (Moscow, 1957).
2. Ya. A. Mandel'baum, N. N. Mel'nikov, V. I. Lomakina, Zhur. Obshchei Khim. 28, 476 (1958).
3. N. N. Mel'nikov, Ya. A. Mandel'baum, Trudy NIUIF 158, 7 (1958).
4. N. N. Mel'nikov, Ya. A. Mandel'baum, V. I. Lomakina, P. V. Popov, USSR Patent 104,225 (1955).
5. N. N. Mel'nikov, Ya. A. Mandel'baum, Z. M. Bakanova, P. G. Zaks, Zhur. Obshchei Khim. 29, 3286 (1959).
6. N. N. Mel'nikov, Ya. A. Mandel'baum, P. G. Zaks, USSR Patent 126,688 (1958).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ORGANIC INSECTOFUNGICIDES

LXII. SYNTHESIS OF SOME NEW DERIVATIVES OF PHOSPHONOACETIC ACID

N. N. Mel'nikov, Ya. A. Mandel'baum, V. I. Lomakina,

and V. S. Livshits

Ya. V. Samoilov Scientific Institute for Fertilizers and Insectofungicides
(NIUIF), Moscow

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3949-3953, December, 1961
Original article submitted January 5, 1961

In connection with a study of the mechanism of the action of various organic phosphorus compounds on insects we recently synthesized in our laboratory a number of derivatives of the dialkoxyphosphonoacetic, -propionic and -butyric acids [1-3], some of which proved to be quite active insecticides. As a continuation of this work, we undertook the synthesis of some amides and amido esters of phosphonoacetic acid, and also of some derivatives of ethoxyphenylphosphonoacetic acid. Synthesis of the phosphonoacetic acid amides was accomplished by the A. E. Arbuzov reaction, involving the reaction of amidophosphites with the esters of monochloroacetic and monochlorothioacetic acids and the amides of monochloroacetic acid, employing conditions similar to those described in the literature [4-9].

$$(C_2H_5O)_2PN(C_2H_5)_2 + ClCH_2COXR' \longrightarrow \begin{matrix} C_2H_5O \\ (C_2H_5)_2N \end{matrix}\!\!>\!P\!<\!\!\begin{matrix} O \\ CH_2COXR' \end{matrix} + C_2H_5Cl$$

$$[(C_2H_5)_2N]_2POC_2H_5 + ClCH_2COXR' \longrightarrow [(C_2H_5)_2N]_2\overset{\overset{O}{\|}}{P}CH_2COXR' + C_2H_5Cl$$

It should be mentioned that the reaction is not entirely smooth, since the presence of a tertiary nitrogen leads to the formation of by-products [10]. The compounds synthesized by us, previously unknown, are listed in the table. A study of the insecticidal properties of these compounds made by P. P. Popov revealed that most of these compounds are weak insecticides. In most cases the LD_{50} for these compounds lies in the range 0.05 to 0.2%.

The derivatives of ethoxyphenylphosphonoacetic acid were also synthesized employing the A. E. Arbuzov method, by reacting the esters of phenylphosphonous acid with the appropriate derivatives of monochloroacetic acid.

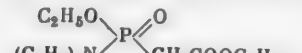
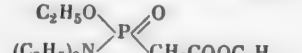
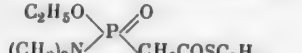
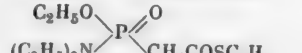
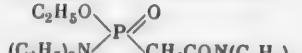
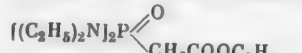
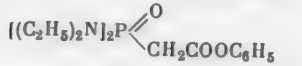
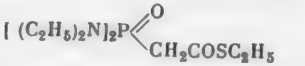
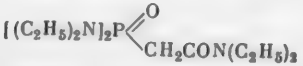
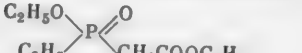
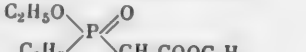
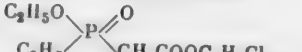
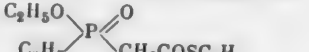
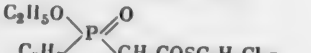
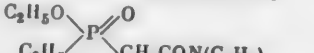
$$C_6H_5P(OC_2H_5)_2 + ClCH_2COXR \longrightarrow \begin{matrix} C_2H_5O \\ C_6H_5 \end{matrix}\!\!>\!P\!<\!\!\begin{matrix} O \\ CH_2COXR \end{matrix} + C_2H_5Cl$$

X = S, N, O.

The obtained compounds and their properties are given in the table.

In insecticidal activity all of the obtained compounds are quite inferior to the previously described esters of phosphonothioacetic acid.

Properties of Derivatives of Phosphonoacetic Acid

Structural formula	B. p. (pressure in mm)	d_4^{20}	n_D^{20}	Yield (in %)	Empirical formula	% P		% N	
						Found	Calcu.	Found	Calcu.
	103—108° (0.4)	1.0599	1.4475	27	$C_{10}H_{22}O_4NP$	11.97, 12.40	12.35	6.03, 6.28	5.58
	162—166 (0.35—0.5)	—	1.4935	16	$C_{14}H_{22}O_4NP$	10.70, 10.71	10.36	4.72, 4.76	4.69
	75—77 (0.15)	1.0894	1.4721	10	$C_8H_{18}O_3NSP$	12.40, 12.52	12.94	5.26, 5.32	5.85
	102—112 (1.3—1.4) *	1.0967	1.4760	16	$C_{10}H_{22}O_3NSP$	12.17, 12.27	11.60	4.61, 4.82	5.24
	158—160 (0.5—1.7) *	1.0440	1.4630	18	$C_{12}H_{27}O_3N_2P$	10.64, 10.58	11.12	9.57, 9.46	10.05
	142—147 (0.45—0.7)	1.0712	1.4668	12	$C_{12}H_{27}O_3N_2P$	10.67, 10.75	11.12	9.86, 9.98	10.05
	160—162 (0.25—0.4)	1.0552	1.4972	10	$C_{16}H_{27}O_3N_2P$	8.90, 8.95	9.50	8.86, 8.84	8.29
	108—113 (0.4) *	1.0473	1.4980	9	$C_{12}H_{27}O_2N_2SP$	11.20, 11.14	10.51	9.42, 9.35	9.52
	139—142 (0.4)	1.0464	1.4775	52	$C_{14}H_{32}O_2N_3P$	9.45, 9.55	10.12	13.88, 13.91	14.40
	142—148 (0.9)	1.1529	1.5078	36.4	$C_{12}H_{17}O_4P$	11.45, 11.70	12.15	—	—
	170—173 (1.1)	1.1570	1.5255	24.0	$C_{16}H_{17}O_4P$	9.65, 9.81	10.08	—	—
	164—170 (0.8)	1.1877	1.5334	21.2	$C_{16}H_{16}O_4PCl$	9.10, 8.70	9.16	—	—
	158—161 (0.4)	1.1651	1.5270	48.5	$C_{12}H_{17}O_3SP$	11.19, 11.46	11.39	—	—
	198—200 (0.6)	1.2361	1.5635	45.5	$C_{16}H_{16}O_3SPCl$	8.27, 8.29	8.97	—	—
	155—160 (0.55)	1.1791	1.5179	17	$C_{14}H_{22}O_3NP$	10.34, 10.65	10.95	—	—

* With partial decomposition.

EXPERIMENTAL

Preparation of amides of phosphonoacetic acid. The amides and the amido esters of phosphonoacetic and phosphonothioacetic acid were obtained under the following typical conditions. Into a flask fitted with a reflux condenser and a mechanical stirrer was charged a solution of the phosphorous acid amido ester in either toluene or xylene (in some cases without a solvent) and then an equivalent amount of the appropriate monochloroacetic acid derivative was added gradually to it with good stirring. When all of the monochloroacetic acid esters or amide had been added, the reaction mixture was heated under reflux for 2-6 hr. When the reaction was run without solvent, the reaction mixture was heated in an oil bath at 150-160° for the indicated length of time. On conclusion of reaction, the solvent was distilled off and the residue was repeatedly fractionated in vacuo.

The obtained compounds and their properties are given in the table.

Preparation of ethoxyphenylphosphonoacetic acid derivatives. A mixture of equimolecular amounts of the ethyl ester of phenylphosphonous acid with either a monochloroacetic or a monochlorothioacetic acid ester, or with a monochloroacetic acid amide, was heated for 2-8 hr in a flask fitted with a reflux condenser and a mechanical stirrer. The temperature of the reaction mixture was held at 140-160°. On conclusion of reaction the product was fractionated in vacuo. The synthesized compounds and their properties are given in the table.

SUMMARY

In order to accumulate some information on the relationship between the insecticidal activity of organic phosphorus compounds and their structure we synthesized a number of previously unknown amides and amido esters of phosphonoacetic and phosphonothioacetic acids, and also of ethoxyphenylphosphonoacetic and -thioacetic acids. Most of the synthesized compounds are weak insecticides.

LITERATURE CITED

1. N. N. Mel'nikov, Ya. A. Mandel'baum, V. I. Lomakina, Zhur. Obshchei Khim. 29, 3289 (1959).
2. N. N. Mel'nikov, Ya. A. Mandel'baum, P. V. Popov, S. L. Varshavskii, V. I. Lomakina, L. P. Kofman, N. S. Ukrainets, USSR Patent 116,879 (1958).
3. N. N. Mel'nikov, Ya. A. Mandel'baum, V. I. Lomakina, Zhur. Obshchei Khim. 31, 849 (1961).
4. A. Michaelis, Lieb. Ann. 326, 161 (1902).
5. Swiss Patents 310,404, 310,412 (1955); C. A. 52, 16684g (1958).
6. A. I. Razumov, Trudy Kazan. Khim.-Tekhnol. Inst. 23, 201 (1957).
7. Brit. Patent 747,824 (1956); C. A. 52, 2048i (1958).
8. J. F. Allen, O. H. Johnson, J. Am. Chem. Soc. 77, 2871 (1955).
9. L. Larsson, Acta Chem. Scand. 6, 1470 (1952).
10. N. N. Mel'nikov, Ya. A. Mandel'baum, K. D. Shvetsova-Shilovskaya, Khim. Sredstva Zashchit. Rastenii, No. 3 5 (1957).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ORGANIC INSECTOFUNGICIDES

LXIII. SYNTHESIS OF SOME PHOSPHINIC ACID DERIVATIVES

N. N. Mel'nikov, Ya. A. Mandel'baum, and Z. M. Bakanova

Ya. V. Samoilov Scientific Institute of Fertilizers and Insectofungicides (NIUIF), Moscow

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 3953-3955, December, 1961
Original article submitted January 11, 1961

It was established recently that many phosphinic acid derivatives have quite a high insecticidal activity with a relatively low toxicity toward warm-blooded animals [1-3]. In this connection it seemed interesting to make a more detailed study of this group of compounds and synthesize a series of new derivatives of various phosphinic acids that have not been described in the literature. As a development of investigations in our laboratory on the relation between insecticidal activity and structure, first of all it seemed interesting to synthesize esters of benzylophosphinic acid containing various substituents in the aromatic radical and also esters of substituted ethylbenzylphosphinic and phenylbenzylphosphinic acids.

These compounds were synthesized by A. E. Arbuzov's reaction of substituted benzyl chlorides with esters of phosphorous, ethylphosphinous, and phenylphosphinous acids.

$$P(OR)_3 + R'CH_2Cl \longrightarrow (RO)_2P(O)CH_2R' + RCl$$

$$RP(OR')_2 + ArCH_2Cl \longrightarrow ArCH_2(R)P(O)OR' + RCl$$

The reaction proceeded relatively readily when a mixture of equimolecular amounts of the starting materials was heated at 160-180°. The compounds we obtained and their properties are given in the table.

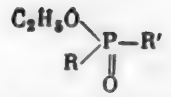
Simultaneously, by an analogous method we synthesized esters of xylylenebis(ethylphosphinic) and xylylenebis-(phenylphosphinic) acids and also an ester of phenylenebis(phenylphosphinic) acid, which could be of interest not only as insecticides and acaricides, but also as bifunctional monomers. These compounds were also synthesized by A. E. Arbuzov's reaction. The compounds obtained are given in the table.

A study of the insecticidal activity of the compounds synthesized, which was carried out by P. V. Popov and N. S. Ukrainets on granary weevils, showed that almost all of the compounds are weakly active and LD_{50} exceeds 0.15%.

EXPERIMENTAL

All the compounds described above were prepared under the following conditions. Into a flask with a reflux condenser and a mechanical stirrer was placed the ester of phosphorous, ethylphosphinous, or phenylphosphinous acid and to it was gradually added the appropriate benzyl halide or xylylene chloride. The reaction mixture was stirred vigorously, heated gradually to 160 or 180°, and kept at this temperature for 2-6 hr. After cooling, the product obtained was fractionated in vacuum. The crystalline substances were recrystallized from an appropriate solvent. The reaction proceeded most readily with substituted benzyl chlorides and with more difficulty with benzyl halides.

The ethyl ester of p-xylylenebis(phosphinic acid) was synthesized by B. A. Arbuzov and B. P. Lugovkin [4, 5]. None of the other compounds have been described in the literature.



Samp. No.	R	R′	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	Yield (%)	Empirical formula	% P found	% P calcu.
1	OC_2H_5	$CH_2-C_6H_4-CH_3$-p *	132—135° (0.7)	1.0760	1.4960	53.5	$C_{12}H_{19}O_3P$	12.60, 12.76	12.80
2	OC_2H_5	$CH_2-C_6H_4-CH_3$-m	126—127 (0.7)	1.0775	1.4950	30	$C_{12}H_{19}O_3P$	12.40, 12.45	12.80
3	OC_2H_5	$CH_2-C_6H_4-CH_2OC_2H_5$-p	124—127 (0.15)	1.0838	1.4920	50	$C_{14}H_{23}O_4P$	10.71, 11.17	10.82
4	OC_2H_5	$CH_2-C_6H_4-CH_2SC_2H_5$-p	174—180 (0.4—0.6)	1.1222	1.5270	35	$C_{14}H_{23}O_3SP$	10.20, 10.24	10.26
5	OC_2H_5	$CH_2-C_6H_4-COOCH_3$-p	137—138.5 (0.15)	1.1751	1.5100	45	$C_{13}H_{19}O_5P$	10.78, 10.65	10.82
6	OC_2H_5	$CH_2-C_6H_4-CH_2P(OC_2H_5)_2$-p **	203—206 (0.1) M. p. 67°	—	—	50	$C_{16}H_{28}O_6P_2$	16.50, 16.41	16.40
7	C_6H_5	$CH_2-C_6H_4-CH_3$-p	158—161 (0.7) M. p. 68—69°	—	—	63	$C_{16}H_{19}O_2P$	11.10, 10.75	11.33
8	C_6H_5	$CH_2-C_6H_4-CH_3$-m	170—173 (1)	1.1141	1.5580	30	$C_{16}H_{19}O_2P$	11.20, 11.10	11.33
9	C_6H_5	$CH_2-C_6H_4-COOCH_3$-p	M. p. 77—78°	—		75.5	$C_{17}H_{19}O_4P$	10.24, 9.90	9.75
10	C_2H_5	$CH_2-C_6H_4-CH_2P(O)(OC_2H_5)(C_2H_5)$-p	M. p. 65°	—	—	29	$C_{16}H_{28}O_4P_2$	17.65, 17.77	17.91
11	C_6H_5	$CH_2-C_6H_4-CH_2P(O)(OC_2H_5)(C_6H_5)$-p	M. p. 151—153.5°	—	—	93.7	$C_{24}H_{28}O_4P_2$	13.78, 14.11	13.99
12		$C_6H_4[P(O)(OC_2H_5)(C_6H_5)]_2$	120—123 (0.5)	1.0989	1.5040	41	$C_{22}H_{24}O_4P_2$	14.79, 14.67	14.97

* Literature data [4, 5]: b. p. 130-133 (2), n_D^{20} 1.4960, d_4^{20} 1.0832.

** Literature data [4, 5]: m. p. 72° and b. p. 204° (2 mm).

The compounds synthesized and their properties are given in the table.

SUMMARY

To look for new active insecticides and accumulate data on the relation between insecticidal activity and the structure of organophosphorus compounds, we synthesized a series of esters of substituted benzylphosphinic, ethylbenzylphosphinic, and phenylbenzylphosphinic acids which have not been described in the literature. The compounds obtained were found to be weak insecticides.

LITERATURE CITED

1. N. N. Mel'nikov, ZhVKhO im. D. I. Mendeleeva 5, 275 (1960).
2. N. N. Mel'nikov, Ya. A. Mandel'baum, V. I. Lomakina, ZhOKh 29, 3289 (1959).
3. R. L. Metcalf, T. R. Fukuto, J. Econ. Entom. 53, 127 (1960).
4. B. A. Arbuzov, B. P. Lugovkin, DAN SSSR 59, 1301 (1948).
5. B. A. Arbuzov, B. P. Lugovkin, Izv. AN SSSR, OKhN 1950, 56.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

X. CYANINE DYES CONTAINING FLUORINE IN THE POLYMETHYNE CHAIN

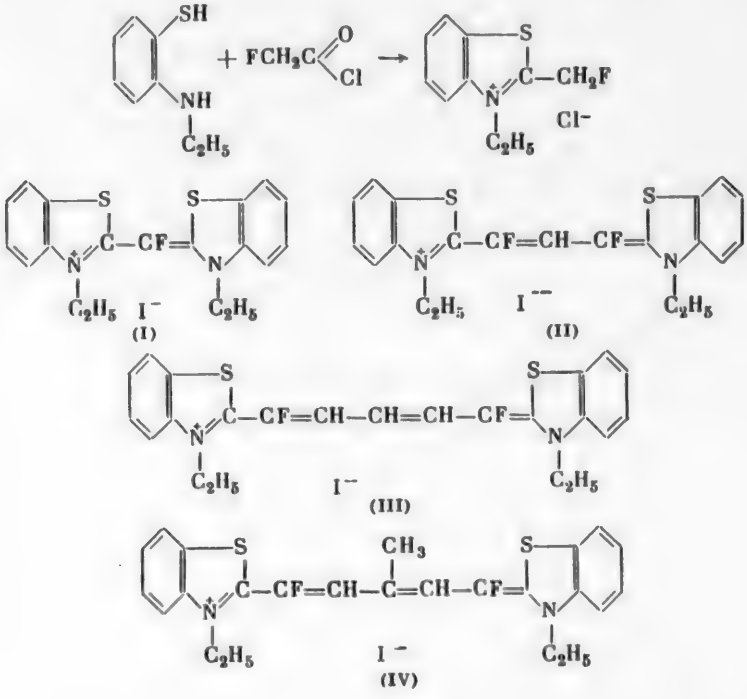
L. M. Yagupol'skii and B. E. Gruz

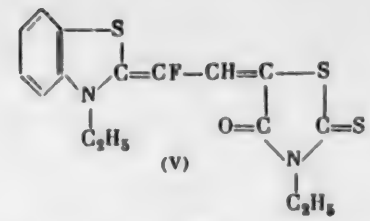
Institute of Organic Chemistry, Academy of Sciences, Ukrainian SSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3955-3961, December, 1961
Original article submitted January 21, 1961

Very few cyanine dyes containing halogen atoms in the polymethyne chain are known. Dicarbocyanines containing chlorine and bromine atoms in the meso-positions of the polymethyne chain [1-3] and a 3,3'-diphenylthiacarbocyanine with bromine atoms in positions 8 and 10 [4] have been synthesized. The replacement of hydrogen by a halogen in these cases has little effect on the position of the absorption maximum of the dyes. Fluorine, chlorine, and iodine atoms have not been introduced into the polymethyne chain of thiacarbocyanine dyes.

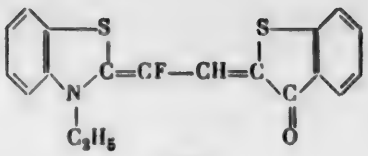
The introduction of fluorine atoms is of particular interest as the synthesis of a new type of dye, namely, fluoropolymethyne dyes, with a large number of different representatives is possible as a result of the high strengths of the fluorine-carbon bond.

We decided to begin the investigation of fluoropolymethyne dyes with the synthesis of thiacarbocyanines containing fluorine atoms in the polymethyne chain. For this purpose, 2-fluoromethylbenzthiazole chloroethylate was synthesized by a known method [5] and used to prepare a monomethynecyanine, carbo- and dicarbocyanines, merocyanines, and a styryl dye by the usual methods.

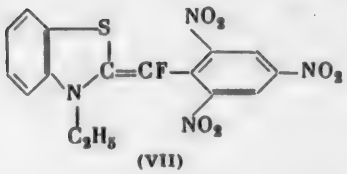




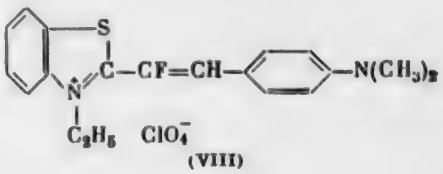
(V)



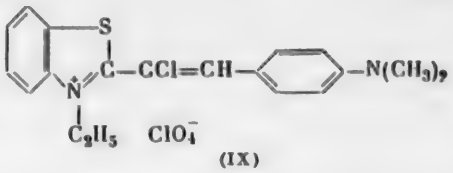
(VI)



(VII)



(VIII)



(IX)

The absorption maxima of the dyes synthesized and their molecular extinctions in alcohol are given in Table 1.

For comparison, Table 1 gives the absorption maxima and molecular extinctions of dyes without fluorine atoms in the chain and also λ_{max} and ε of some dyes containing methyl groups instead of fluorine atoms.

We attempted to prepare for comparison dyes containing chlorine atoms in the polymethyne chain from the quaternary salt 2-chloromethylbenzthiazole chloroethylate, which has been described previously [9]. However, the thiacarbocyanine synthesized did not correspond in analysis to 8,10-dichlorothiacarbocyanine. It was possible to obtain only the styryl dye (IX).

As the data in Table 1 show, the introduction of fluorine atoms into the polymethyne chain produces a considerable displacement of the absorption band of the dye into the long-wave part of the spectrum, which is greater than that produced by a methyl group (apart from the monomethynecyanine I).

TABLE 1. Absorption Maxima of Dyes Synthesized

Sample No.	λ_{max} (mμ)	$\varepsilon \cdot 10^4$	For dye without F in chain		Displacement of λ_{max} in comparison with dye without sub. in chain (mμ)	For dye with CH_3 group instead of fluorine atom in chain	
			λ_{max} (mμ)	$\varepsilon \cdot 10^4$		λ_{max} (mμ)	$\varepsilon \cdot 10^4$
(I)	453	6.33	425	7.5 [6]	31	480	4.3 [6]
(II)	605	11.52	558 *	14.0 [6]	47	570 *	7.0 [6]
(III)	703	13.85	652 *	19.9 [7]	51		
(IV)	715	14.8	651 *	21.8 [7]	65		
(V)	551 **	6.32	524	11.31 [8]	27	540	11.29 [8]
(VI)	589 ***	8.0	554		35	574	
(VII)	625 ****	1.41	552 *	3.0 [9]	73	605 *	1.25 [9]
(VIII)	532	6.55	530	11.0 [10]	2	481	6.2 [10]
(IX)	508	1.88	530	11.0 [10]	22	481	6.2 [10]

* The data given are for the dye with methyl groups at the nitrogen atoms.

** In benzene λ_{max} 537 mμ.

*** In benzene λ_{max} 564 mμ.

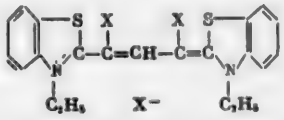
**** In benzene.

The effect of substitutents in the meso-position of the polymethyne chain on the color of thiacarbocyanines has been studied quite thoroughly. Electropositive substituents produce a displacement in the absorption band of the dye into the short-wave part of the spectrum {the CH_3 group by 15 mμ, OCH_3 by 60 mμ and $(C_2H_5)_2N$ by 90 mμ [11]} and electronegative substitutents produce a displacement into the long-wave part of the spectrum (CN group by 62 mμ, NO_2 by 17 mμ, and $COOC_2H_5$ by 14 mμ [12]). Substituents in positions 8 and 10 have the opposite effect, as is shown by the data in Table 2.

Fluorine atoms in the polymethyne chain affect the absorption of the dye analogously to the strong electron-donor substituents given in Table 2. This agrees with the fact that fluorine shows a considerable electron-donor conjugation effect in aromatic compounds [15]. The polmethyne chain may be regarded as an aromatic system. The introduction of fluorine into the polymethyne chain evidently does not reduce, but on the contrary, increases the bascity of the dye.

Using A. I. Kiprianov and L. S. Pupko's method [16], for the dye (II) we determined the value of A, i.e., the concentration of hydrogen chloride (M) in an aqeuous alcohol solution of the dye required to decrease the intensity of the color by a factor of two. The thiacarbocyanine (II) was decolorized quite readily. The value of A was found

TABLE 2. Effect of Substituents on the Color of Thiacarbocyanines



Substituent X	λ_{max} (mμ)	Displacement of λ_{max} in comparison with the dye without a substituent in the chain (mμ)
H	558	-
CH_3	570[6]	12*
$CH_3OC_6H_4$	591[13]	33
OCH_3	597[13]	39
O^-	606[14]	48

*The data given are for the dye with CH_3 groups at the nitrogen atoms.

to equal 0.65, i.e., the basicity of the dye (II) exceeds that of the dye from 4-methylthiazole (A = 0.90), which is quite a strong base.

Steric hindrance created by the fluorine atoms evidently also has some effect on the color of the dyes. This is indicated by the fall in the molecular extinction of dyes containing fluorine in the polymethyne chain in comparison with dyes with no substituents in the chain. As the data in Table 1 show, bulky methyl groups produce an even greater in the extinction. Like other sterically "hindered" dyes [6], the thiacarbocyanine (II) was decolorized almost instantly by the addition of 0.01 N alkali solution.

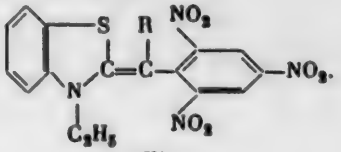
Thus, the reason for the displacement of the absorption band toward long wavelengths with thiacyanines and merocyanines containing fluorine atoms in the polymethyne chain is the superposition of two effects acting in the same direction, namely, the effect of electron-donor conjugation of the substituent and steric hindrance. The first factor is evidently of predominant importance in the given case.

These effects act in opposite directions in styryl dyes: steric hindrance produces a hypsochromic displacement [10] and electron-donor conjugation with the dimethylamino group should lead to a bathochromic displacement. This results in the fact that fluorine has hardly any effect on the color of the dye, while the chlorine, which is larger, like the methyl group, displaces the absorption maximum of the styryl toward short wavelengths.

TABLE 3. Decolorization of Thiacarbocyanine (II) by Hydrochloric Acid

Degree of decolorization (%)	HCl concentration (M)	A
14.05	0.0697	
30	0.232	0.65
51	0.697	

The predominant importance of the electronic effect of the substituent explains the change in the color of nonsaltlike dyes of the type



(X)

TABLE 4. Effect of Substitutents on the Color of Dyes of the Type (X)

R	H	Cl	CH_3	F
λ_{max} (mμ) (In benzene)	552[9]	605[9]	610[9]	625

EXPERIMENTAL

2-Fluoromethylbenzthiazole chloroethylate. A solution of 4.6 g of N-ethylamino-o-thiophenol in 5 ml of benzene was added dropwise with cooling and stirring to 4 g of fluoroacetyl chloride in 5 ml of benzene. An oily layer rapidly settled and 10 min after the end of the reaction, it solidified. The quaternary salt was collected, washed with benzene and ether, and dried in a vacuum desiccator. The yield of the crude product was 6.9 g (quantitative). The preparation was purified by solution in a small amount of alcohol and the dropwise addition of ether until crystallization began. The recrystallization from a mixture of alcohol and ether was repeated for analysis. The white needles had m. p. 181-182° (decomp.).

Found %: N 5.82, 5.93; Cl 15.08, 15.25. $C_{10}H_{11}NSFCl$. Calculated %: N 6.04; Cl 15.33.

Bis[3-ethylbenzthiazole-(2)]-8-fluoromethynecyanine iodide (I). A mixture of 0.25 g of 2-fluoromethylbenzthiazole chloroethylate and 0.38 g of 3-ethyl-2-methylmercaptobenzthiazole tosylate was heated with 1 ml of dry pyridine at 60° for 30 min and at 100° for 15 min. The mixture was diluted with water, the dye collected and dissolved in methanol, and the iodide precipitated with an aqueous solution of potassium iodide. The yield was 0.21 g (43.5%). The yellow needles had m. p. 233-234° (from alcohol).

Found %: F 4.18, 4.23; I 25.97, 26.10. $C_{19}H_{18}N_2S_2FI$. Calculated %: F 3.93; I 26.27.

Bis[3-ethylbenzthiazole-(2)]-8,10-difluoromethynecyanine iodide (II). A mixture of 0.5 g of 2-fluoromethylbenzthiazole chloroethylate, 0.5 g of orthoformic ester, and 3.5 ml of acetic anhydride was boiled for 10 min. The dye was precipitated with ether, collected, dissolved in 20 ml of alcohol, and precipitated with an aqueous solution of potassium iodide. The precipitated dye was washed with water, alcohol, and ether. The yield was 0.21 g (40%). After two recrystallizations from alcohol, it formed large emerald crystals with m. p. 218° (decomp.)

Found %: F 7.20, 7.45; I 24.40, 24.47; N 5.29, 5.32. $C_{21}H_{19}N_2S_2F_2I$. Calculated %: F 7.20; I 24.05; N 5.30.

Bis[3]ethylbenzthiazole-(2)]-8,12-difluoropentamethynecyanine iodide (III). A mixture of 0.5 g of 2-fluoromethylbenzthiazole chloroethylate, 0.2 g of the dianil of malonic aldehyde, 0.5 ml of triethylamine, and 5 ml of acetic anhydride was heated on a boiling water bath for 30 min. The dye was precipitated with ether, collected, washed with ether and water, and dissolved in alcohol and the iodide precipitated with an aqueous solution of potassium iodide. The yield was 0.27 g (47%). Recrystallization from methanol gave 0.09 g of the dye.

Found %: F 6.68, 6.43. $C_{23}H_{21}N_2S_2F_2I$. Caluclated %: F 6.87.

Bis[3-ethylbenzthiazole-(2)]-8,12-difluoro-10-methylpentamethynecyanine iodide (IV). A mixture of 0.4 g of 2-fluoromethylbenzthiazole chloroethylate, 0.2 g of the dianil of methylmalonic aldehyde, 0.4 ml of triethylamine, and 4 ml of acetic anhydride was heated on a boiling water bath for 30 min. Subsequent treatment was as in the preparation of the dye (III). The yield was 0.085 g (18.7%). Recrystallization from alcohol gave 0.035 g of the dye with m. p. 182-183° (decomp.).

Found%: F 6.31, 6.37. $C_{24}H_{23}N_2S_2F_2I$. Calculated % F 6.69.

3-Ethyl-5-[3'-ethylbenzthiazolinylidene-2'-(β-fluoroethylidene-2)]-thiazolinethion-(2)-one-(4) (V). A mixture of 0.25 g of 2-fluoromethylbenzthiazole chloroethylate, 0.31 g of the acetovinyl derivative of N-ethylrhodanine, and 2 ml of pyridine was heated at 115° on a glycerol bath for 20 min. The mixture was cooled and diluted with water and the dye collected and washed with hot water, alcohol, and ether. The yield was 0.21 g (56.3%). The product was recrystallized from glacial acetic acid and washed with ether to yield 0.16 g of dye with m. p. 237-238°.

Found %: F 5.36, 5.46; S 26.36; 26.47. $C_{16}H_{15}ON_2S_3F$. Calculated %: F 5.20; S 26.12.

2-[3'-Ethylbenzthiazolinylidene-2'-(β-fluoroethylidene-2)-3-oxo-2,3-dihydrothionaphthene (VI). A mixture of 0.15 g of 2-fluoromethylbenzthiazole chloroethylate, 0.15 g of the anil of β-hydroxythianaphthene-2-aldehyde, 0.12 ml of triethylamine, and 4 ml of pyridine was heated on a boiling water bath for 10 min and boiled for 10 min. After cooling, the reaction mixture was diluted with water. The dye was collected and washed with water, alcohol, and ether. The yield was 0.17 g (80%). The dye was recrystallized from alcohol to yield 0.05 g of product with m. p. 220-222° (decomp.).

Found %: F 5.15, 5.65. $C_{19}H_{14}ONS_2F$. Calculated %: F 5.35.

3-Ethyl-2-(2',4',6'-trinitrophenyl)-fluoromethylenebenzthiazoline (VII). A solution of 1 ml of triethylamine in 3 ml of anhydrous alcohol was added dropwise to a solution of 0.3 g of 2-fluoromethylbenzthiazole chloroethylate and 0.3 g of picryl chloride in 12 ml of anhydrous alcohol at 5°. A dark green, finely crystalline dye precipitated immediately. The yield was 0.26 g (49%). The product was washed with 20 ml of cold alcohol. The dye was almost insoluble in methanol, readily soluble in benzene, nitromethane, and dioxane, and difficulty soluble in ether. It contained a molecule of alcohol and had m. p. 115-116° (decomp.).

Found %: F 4.20, 4.24; N 12.66, 12.78. $C_{16}H_{11}O_6N_4SF \cdot C_2H_5OH$. Calculated %: F 4.20; N 12.40.

3-Ethyl-2-p-dimethylamino-β-fluorostyrylbenzthiazole perchlorate (VIII). A mixture of 0.2 g of 2-fluoromethylbenzthiazole chloroethylate and 0.15 g of p-dimethylaminobenzaldehyde was fused on a boiling water bath for 1.5 hr, connected to vacuum, and heated for a further 10 min at 115°. The dye was washed with ether, dissolved in alcohol, and precipitated with an aqueous solution of sodium perchlorate. The yield was 0.16 g (45%) and the m. p. 182-183° (from alcohol).

Found %: F 4.65, 4.86; N 6.52; 6.64. $C_{19}H_{20}O_4N_2SFCl$. Calculated %: F 4.46; N 6.56.

3-Ethyl-2-p-dimethylamino-β-chlorostyrylbenzthiazole perchlorate (IX). A mixture of 0.3 g of 2-chloromethylbenzthiazole chloroethylate [5], 0.2 g of p-dimethylaminobenzaldehyde, and 2.5 ml of acetic anhydride was boiled for 20 min. After the mixture had cooled, the dye was precipitated with ether, dissolved in alcohol, and precipitated with an aqueous solution of sodium perchlorate. The precipitated dye was collected, washed repeatedly with hot water, and recrystallized from methanol. It formed long blue needles with a metallic luster. The yield was 0.26 g (50%) and the m. p. 220-221°.

Found %: Cl 16.07, 16.10; N 6.29, 6.15. $C_{19}H_{20}O_4N_2SCl_2$. Calculated %: Cl 16.02; N 6.32.

SUMMARY

1. The synthesis of the first representatives of a new type of dye, namely, fluoropolymethyne dyes, is described. A monomethynecyanine, carbo and dicarbocyanines, merocyanines, and a styryl dye containing fluorine in the polymethyne chain were prepared.

2. It was shown that the introduction of fluorine atoms into the polymethyne chain of thiacarbocyanines and merocyanines produces a considerable displacement of the absorption maximum of the dyes toward long wavelengths (by 30-60 mμ).

LITERATURE CITED

1. S. Beattie, I. M. Heilbron, F. Irving, J. Chem. Soc. 1932, 260.
2. Z. P. Sytnik, B. S. Shteingardt, ZhPKh 9, 1842 (1936).
3. A. T. Troshchenko, ZhOKh 9, 1661 (1939).
4. A. I. Kiprianov, I. K. Ushenko, ZhOKh 17, 2201 (1947).
5. A. I. Kiprianov, Z. N. Pazenko, ZhOKh 19, 1515 (1949).
6. A. I. Kiprianov, I. K. Ushenko, Izv. AN SSSR, OKhN 1950, 492.
7. G. E. Ficken, I. D. Kendall, J. Chem. Soc. 1959, 3988.
8. M. V. Deichmeister, Z. P. Sytnik, I. I. Levkoev, É. B. Lifshits, ZhOKh 24, 898 (1954).
9. L. M. Yagupol'skii, M. S. Marenets, ZhOKh 23, 481 (1953).
10. A. I. Kiprianov, I. K. Ushenko, ZhOKh 20, 514 (1950).
11. N. N. Sveshnikov, I. I. Levkoev, B. S. Portnaya, É. B. Lifshits, DAN SSSR 84, 733 (1952).
12. A. I. Kiprianov, Yu. S. Rozum, Sb. rabot Instituta organicheskoi khimii AN USSR 13, 29 (1947).
13. A. I. Kiprianov, Zh. M. Ivanova, S. G. Fridman, Ukr. khim. zh. 20, 641 (1954).
14. V. M. Zubarovskii, ZhOKh 21, 1063 (1951).
15. Steric Effects in Organic Chemistry [Russian translation] IL, 595 (1960).
16. A. I. Kiprianov, S. G. Fridman, L. S. Pupko, Sb. rabot IOKh AN USSR 13, 40 (1947).

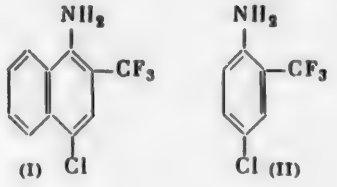
All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

2-TRIFLUOROMETHYLNAPHTHALENE AND ITS DERIVATIVES. II

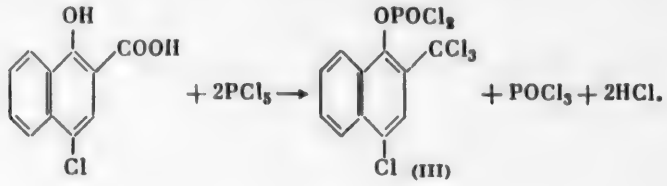
L. M. Yagupol'skii, Yu. A. Fialkov, and P. A. Yufa

Institute of Organic Chemistry, Academy of Sciences, Ukrainian SSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3962-3970, December, 1961
Original article submitted January 3, 1961

The synthesis of 1-chloro, 1-carboxy, and 1-amino derivatives of 2-tri-fluoromethylnaphthalene was described in a previous communication [1]. The present work was undertaken to prepare 1-amino-2-trifluoromethyl-4-chloro-naphthalene (I), an analog of one of the best azo amines, namely, Brilliant ruby J (II).



For the synthesis of derivatives of 1-chloro-2-trifluoromethylnaphthalene substituted in position 4, the reaction of the corresponding 1-hydroxy-2-naphthoic acids with phosphorus pentachloride was studied. The reaction of 1-hydroxy-4-chloro-2-naphthoic acid with 2 moles of phosphorus pentachloride formed a compound whose analysis corresponded to the formula $C_{11}H_6O_2PCl_6$. In analogy with the product isolated from the reaction of 1-hydroxy-2-naphthoic acid with phosphorus pentachloride [2], we assigned structure (III) to this compound. It is formed according to the scheme



(A)

The treatment of (III) with 1 mole of phosphorus pentachloride in a sealed tube at 180° formed 1,4-dichloro-2-trichloromethylnaphthalene (IV). The latter compound could be obtained from 1-hydroxy-4-chloro-2-naphthoic acid in one stage by heating with 3 moles of phosphorus pentachloride at 180°. The yield of (IV) was increased in this case.

When 1-hydroxy-4-nitro-2-naphthoic acid [3] was heated with phosphorus pentachloride even at 140°, the evolution of nitrogen oxides began. 1,4-Dichloro-2-trichloromethylnaphthalene was formed as a result of this reaction.

1-4-Dichloro-2-trichloromethylnaphthalene was fluorinated by boiling with antimony trifluoride in dioxane or chlorobenzene. The reaction time was varied from 6 to 12 hr; both the starting material and partial fluorination products were isolated. 1,4-Dichloro-2-trifluoromethylnaphthalene (V) could be isolated in 75% yield by heating (IV) with antimony trifluoride without a solvent. Much better exchange of chlorine for fluorine occurred with anhydrous hydrofluoric acid; the yield of (V) reached 98%.

It is interesting to note that the introduction of a chlorine atom into position 4 of 1-chloro-2-trichloromethylnaphthalene hampers fluorination. Thus, (IV) exchanges the chlorine in the trichloromethyl group for fluorine with antimony trifluoride or hydrofluoric acid only at 150°, while 1-chloro-2-tri-chloromethylnaphthalene does so at 130°.

1,4-Dichloro-2-trifluoromethylnaphthalene did not react with an aqueous or aqueous alcohol solution of ammonia in the presence of metallic copper or its salts when heated without stirring in a sealed ampoule at 200°. Likewise, an amino derivative could not be obtained with sodamide in liquid ammonia. An attempt to replace the chlorine atom in position 1 by a cyano group by heating with cuprous cyanide in pyridine was unsuccessful. After the reaction mixture had been heated at 190° for 20 hr, the starting material was recovered. Increasing the temperature to 230-240° led to tar formation. Equally unsuccessful were attempts to replace the chlorine by an amino group in 1-chloro-2-trifluoromethylnaphthalene with aqueous, alcohol and aqueous alcohol solutions of ammonia under the same conditions as in the previous case and also with potassium phthalimide by boiling for 16 hr in dimethylformamide. The starting material was recovered in all cases; 1-amino-2-trifluoromethylnaphthalene was obtained therefore by a method described previously [1]. Its chlorination with N,N'-dichlorourea even in the cold led to tar formation. N-Chlorosuccinimide in carbon tetrachloride did not react with 1-amino-2-trifluoromethylnaphthalene either when the mixture was boiled for 2 hr. Treatment of an acetic acid solution of the amine with a solution of chlorine in acetic acid in the cold formed a product with decomp. point ~140°, which was evidently the N-chloro derivative. Boiling it in ligroin gave a 22% yield of 1-amino-4-chloro-2-trifluoromethylnaphthalene. It is interesting to note that the starting amine was isolated when the N-chloro derivative was heated in benzene. Chlorination of the benzene probably occurred. The structure of (I) was demonstrated by replacement of the amino group by chlorine by Sandmeyer's method. The reaction product did not depress the melting point of 1,4-dichloro-2-trifluoromethylnaphthalene.

We were able to obtain 1-amino-4-chloro-2-trifluoromethylnaphthalene in a high yield by treatment of 1-amino-2-trifluoromethylnaphthalene with sulfuryl chloride in carbon tetrachloride. The N-chloro derivative formed was isolated and rearranged into (I) by boiling in ligroin. Bromination of 1-amino-2-tri-fluoromethylnaphthalene with a solution of bromine in acetic acid formed the N-bromo derivative. When boiled in benzene, it rearranged into 1-amino-4-bromo-2-trifluoromethylnaphthalene. In contrast to the case of the N-chloro derivative, the rearrangement proceeded smoothly and was not accompanied by halogenation of the solvent.

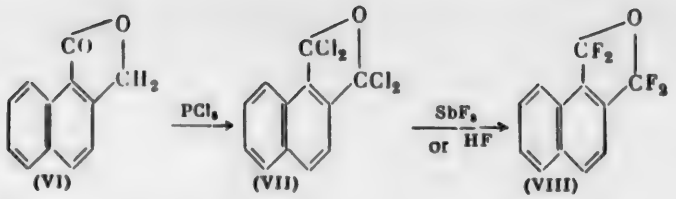
When acetylated with excess acetic anhydride in the presence of sulfuric acid, 1-amino-2-trifluoromethylnaphthalene and its 4-chloro derivative readily formed N,N-diacetyl derivatives. Boiling the latter with 20% hydrochloric acid yielded monoacetyl compounds.

It was not possible to obtain the diacetyl derivative of (I) by chlorination of 1-diacetylamino-2-trifluoromethylnaphthalene with chlorine in acetic acid and chloroform, N-chlorosuccinimide, potassium chlorate in hydrochloric acid, and sulfuryl chloride in carbon tetrachloride.

When treated with a solution of chlorine in acetic acid, 1-acetylamino-2-trifluoromethylnaphthalene formed 1-acetylamino-4-chloro-2-trifluoromethylnaphthalene.

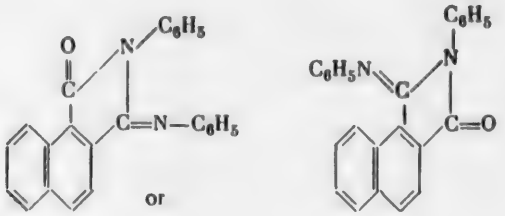
It seemed interesting to prepare the difficulty accessible 2-trifluoromethylnaphthalene in one stage by replacement of the chlorine in 1-chloro-2-trifluoromethylnaphthalene by hydrogen on Raney nickel in alcoholic potassium hydroxide in the cold [4]. After the absorption of 1 mole of hydrogen in the presence of 1 equiv. of potassium hydroxide, the Raney nickel was removed by filtration and the alcohol evaporated. The low-melting mixture of products formed was washed with water; fluorine ions were detected in the aqueous solution in addition to chlorine ions. In the given case there was evidently parallel replacement of chlorine and fluorine by hydrogen. In the reduction of 1-chloro-2-trifluoromethylnaphthalene in the presence of excess alcoholic alkali, 4 moles of hydrogen was absorbed. The product isolated after the reaction was found to be β-methylnaphthalene. Thus, in the given case there is an unusual replacement of fluorine by hydrogen in a very stable trifluoromethyl group attached to an aromatic nucleus.

Tetrachlorophthalane is known to isomerize on heating to form the acid chloride of o-trichloromethylbenzoic acid [5]. In order to prepare trichloromethyl derivatives of naphthalene, it seemed interesting to synthesize α,β-(1,1,3,3-tetrachloro)naphthalane (VII), which has not been described in the literature. For this purpose we prepared naphthalide (VI) [6], which was treated with phosphorus pentachloride to give (VII). The latter was converted into tetrafluoronaphthalane (VIII) by fluroination with antimony trifluoride with heating and also with anhydrous hydrogen fluoride in the cold.



(VI) (VII) (VIII)

To determine the ratio of tetrachlorophthalane and o-trichloromethylbenzoyl chloride in a study of their isomerization, Ott [5] used the reaction with aniline in benzene. Tetrachlorophthalane does not react with a benzene solution of aniline in the cold in 1 hr, while o-trichloromethylbenzoyl chloride forms the anilide quantitatively. In order to confirm the structures of (VII) and (VIII), we studied their reactions with aniline and ammonia. It was found that they do not react in benzene solution with aniline and ammonia over a period of 3 days at 20°. When boiled with a benzene solution of aniline for 5 hr, the tetrachloronaphthalane was converted into a yellow substance with m. p. 213-214°, which, in analogy with the reaction products of tetrachlorophthalane and aniline in benzene [5], may have the structure



Tetrafluoronaphthalane did not react when boiled for 1 hr with aniline in benzene.

It seemed interesting to study the reaction of aniline and ammonia with the acid chlorides of 2-trichloromethyl- and 2-trifluoromethyl-1-naphthoic acids. For this purpose, 2-trifluoromethyl-1-naphthoic acid [1] was converted into the acid chloride (IX). The latter did not react with aniline in benzene solution at room temperature in 1 hr (the starting acid chloride was recovered quantitatively). Boiling (IX) with excess aniline in benzene for 1.5 hr gave the corresponding anilide in almost quantitative yield. When ammonia was passed into a solution of(IX) in ligroin for 3 hr at room temperature, the amide was formed in only 10% yield. These facts must be explained by the steric effect of the trifluoromethyl group. The steric hindrance created by the trichloromethyl group must be still greater. Therefore, the reaction with aniline in benzene is unsuitable for establishing a ratio of the isomeric tetrachloronaphthalane and 2-trichloromethyl-1-naphthoyl chloride (X).

An attempt to prepare (X) from 2-trifluoromethyl-1-naphthoyl chloride by replacement of the fluorine by chlorine with aluminum chloride was unsuccessful. Tetrachloronaphthalane was obtained instead of (X). This was confirmed by the fact that a mixed melting point with an authentic sample of tetrachloronaphthalane was not depressed and by the identity of the ultraviolet spectra of these compounds. Aluminum chloride evidently first replaces the fluorine atoms by chlorine in the trifluoromethyl group and then produces isomerization.

The structure of the tetrafluoronaphthalane should be regarded as established as it did not change when boiled with aniline in benzene, while 2-tri-fluoromethyl-1-naphthoyl chloride formed the anilide quantitatively under these conditions.

The reaction of the tetrachloronaphthalane (VII) with hydrogen fluoride proceeded very readily in the cold. Tetrafluoronaphthalane was obtained in almost quantitative yield. Fluorination of tetrachlorophthalane with hydrofluoric acid in the cold gave only a 70% yield of tetrafluorophthalane, which did not differ in boiling point or refractive index from that obtained previously [7]. As hydrogen fluoride does not produce isomerization in the replacement of chlorine by fluorine in tetrachlorophthalane and tetrachloronaphthalane, it must be assumed that tetrachloronaphthalane has the structure (VII). In the fluorination of tetrachlorophthalane and tetrachloronaphthalane with excess hydrogen fluoride in the cold, small amounts of the diacid fluorides of phthalic and 1,2-naphthalenedicarboxylic acids were formed as by-products as a result of partial hydrolysis of the starting chloro derivatives by

moisture present in the hydrogen fluoride. The presence of these by-products in the fluorination products was confirmed by reactions with ammonia and aniline.

After tetrachloronaphthalane had been heated at 200° for 10 hr, 70% of the substance was recovered unchanged. It was not possible to detect isomerization products, namely, acid chlorides of 1- or 2-trichloromethylnaphthoic acids, in the tarry residue.

The absorption spectrum of tetrachloronaphthalane (VII) in n-hexane (maxima of absorption bands at 235, 257, 278, 286 mμ), like that of tetrachlorophthalane, is displaced toward longer wavelengths in comparison with that of tetrafluoronaphthalane (VIII) (maxima of absorption bands at 224, 242, 256, 273 and 280 mμ).

EXPERIMENTAL

1,4-Dichloro-2-trichloromethylnaphthalene. a) A mixture of 13.4 g of 1-hydroxy-4-chloro-2-naphthoic acid [8], 28.4 g of phosphorus pentachloride, and 2 ml of phosphorus oxychloride was heated at 90-100° for 1.5 hr. Toward the end of the reaction, which was indicated by a fall in the evolution of hydrogen chloride, the temperature was raised to 110° and the mixture heated for 15-20 min. The hydrogen chloride was absorbed in water. The amount of hydrogen chloride liberated was 95% (according to scheme A). The excess phosphorus pentachloride and phosphorus oxychloride were removed in a water-pump vacuum on a water bath and the residue was treated with an equal volume of ligroin, heated to boiling, filtered rapidly, and left to crystallize. The product was collected, washed with ligroin, and dried in a vacuum desiccator over phosphorus pentoxide. The yield was 18.9 g (76%) and the m. p. 83-85°.

Found: Cl 51.29, 51.33. Equiv. (after hydrolysis) 7.83, 7.95. $C_{11}H_5O_2PCl_6$. Calculated %: Cl 51.57. Equiv. 8.00.

A mixture of 5.4 g of the product from the previous stage and 3.4 g of phosphorus pentachloride was heated at 180° for 3 hr in a sealed tube. The phosphorus oxychloride and excess phosphorus pentoxide were removed in a water-pump vacuum on a boiling water bath and the residue extracted with ether, washed with water, 5% sodium carbonate solution, and water, and dried. The ether was removed and the product recrystallized from acetone. The yield was 2.3 g (56%, calculated on the product from the first stage or 43%, on the 1-hydroxy-4-chloro-2-naphthoic acid). The needles had m. p. 103-104° (from a mixture of benzene and methanol).

Found %: Cl 56.25, 56.33. $C_{11}H_5Cl_5$. Calculated %: Cl 56.44.

b) A mixture of 44.5 g of 1-hydroxy-4-chloro-2-naphthoic acid and 150 g of phosphorus pentachloride was heated slowly to 130° on an oil bath over a period of 2 hr and the phosphorus oxychloride distilled simultaneously. The bath temperature was then raised to 180° and kept at this for 3 hr. The remaining phosphorus oxychloride and phosphorus pentoxide were removed in a water-pump vacuum on a boiling water bath. The contents of the flask were treated with iced water and extracted with ether. The ether layer was washed with water and sodium carbonate solution. The ether was removed and the residue recrystallized from a mixture of methanol and benzene. The yield was 36 g (57%) and the m. p. 102-103°. The preparation did not depress the melting point of the 1,4-dichloro-2-trichloromethylnaphthalene described above.

1,4-Dichloro-2-trifluoromethylnaphthalene. a) A mixture of 31.5 g of 1,4-dichloro-2-trichloromethylnaphthalene and 36 g of antimony trifluoride was stirred at 150° (in the bath) for 2 hr. The mixture was treated with 20% hydrochloric acid and the product extracted with ether. The ether layer was washed with 20% hydrochloric acid for the removal of antimony salts, with water, 2% sodium carbonate solution, and water and dried. Removal of the ether yielded 20 g (75%) of 1,4-dichloro-2-trifluoromethylnaphthalene. The needles had m. p. 75-76° (from ligroin).

Found %: Cl 26.33, 26.44; F 21.69, 21.79. $C_{11}H_5F_3Cl_2$. Calculated %: Cl 26.78; F 21.51.

In one fluorination experiment, which was carried out in a flask of Jena glass, strong corrosion of the surface was observed. In addition to the trifluoromethyl derivative, the reaction products contained the acid fluoride of 1,4-dichloro-2-naphthoic acid, which was evidently formed by hydrolysis of 1,4-dichloro-2-trichloromethylnaphthalene and fluorination of the acid chloride. The acid fluoride precipitated first in the recrystallization of the fluorination product from ligroin. It did not decompose when stored for a long time in air. The needles had m. p. 128-130°.

Found %: Cl 29.20, 29.35. $C_{11}H_5OFCl_2$. Calculated %: Cl 29.17

b) Into a 120-ml stainless steel autoclave, fitted with a pressure gauge and valve for the release of pressure, were placed 9.43 g of 1,4-dichloro-2-trichloromethylnaphthalene and 18.0 g of hydrogen fluoride. The mixture was heated for 8 hr at 150° (in the bath). The pressure in the autoclave reached 30 atm. The autoclave was cooled with iced water and the excess pressure released through the valve. The excess hydrogen fluoride was removed by distillation and the product remaining in the autoclave treated with water and 5% potassium hydroxide solution. The product was collected, washed with water, and dried. The yield was 7.8 g (98%) and the m. p. 74-75°. The preparation did not depress the melting point of the 1,4-dichloro-2-trifluoromethylnaphthalene described above.

1-Chloro-2-trifluoromethylnaphthalene. Into an autoclave were placed 28.0 g of 1-chloro-2-trichloromethylnaphthalene and 60.0 g of hydrogen fluoride. The mixture was heated for 6 hr at 130° (in the bath), when the pressure in the autoclave reached 65 atm. The product was treated as described above and steam distilled. The yield was 21.0 g (91%) and the m. p. 58-59°. The preparation did not depress the melting point of the 1-chloro-2-trifluoromethylnaphthalene obtained previously [1].

1-Amino-4-chloro-2-trifluoromethylnaphthalene. A 3.2 g-sample of 1-amino-2-trifluoromethylnaphthalene was dissolved in 15 ml of dry carbon tetrachloride. Part of the solvent was evaporated for the complete removal of moisture. The solution was cooled in iced water and a solution of 2.05 g of sulfuryl chloride in 4 ml of dry carbon tetrachloride added dropwise with stirring. After a few minutes, heating of the mixture was begun, the temperature gradually raised to 80°, then the mixture allowed to cool and chilled in iced water, and the precipitated product collected after 10 min. The product was washed on the filter with dry carbon tetrachloride and pressed out carefully. It was dried for 30 min in vacuum over P_2O_5, then mixed with 50 ml of dry ligroin with b. p. 50-55°, and boiled until it dissolved. The hot solution was filtered and evaporated to dryness in a water-pump vacuum on a water bath. The yield was 2.9 g (79%) and the needles had m. p. 57.5-59° (from ligroin).

Found %: Cl 14.28, 14.33. $C_{11}H_7NF_3Cl$. Calculated %: Cl 14.44.

1-Amino-4-bromo-2-trifluoromethylnaphthalene. A solution of 0.48 g of bromine in 6 ml of glacial acetic acid was added with stirring and cooling with water to a solution of 0.63 g of 1-amino-2-trifluoromethylnaphthalene in 4 ml of glacial acetic acid. After 30 min the precipitated crystals of the N-bromo derivative were collected, pressed out carefully, and washed with glacial acetic acid (decomp. p. 168-171°). The product was mixed with 40 ml of dry benzene and boiled until it dissolved, the solution filtered, and the benzene removed in a water-pump vacuum. The yield was 0.69 g (79%) and the needles had m. p. 65-66° (from aqueous alcohol).

Found %: Br 17.66, 27.99. $C_{11}H_7NF_3Br$. Calculated %: Br 27.55.

1-(N,N-Diacetylamino)-2-trifluoromethylnaphthalene. To a mixture of 2.1 g of 1-amino-2-trifluoromethylnaphthalene and 7.5 ml of acetic anhydride was added 1 drop of concentrated sulfuric acid and the mixture heated on a water bath for 1 hr. The product was poured into water, 2.5 g of sodium acetate added, and the mixture stirred, heated to 80°, and left overnight. The crystals of the diacetyl derivative were collected, washed with water, and recrystallized from aqeuous alcohol. The yield was 2.2 g (75%) and the needles had m. p. 109.5-111.5°.

Found %: N 4.85, 4.91. $C_{15}H_{12}O_2NF_3$. Calculated %: N 4.75.

1-(N,N-Diacetylamino)-4-chloro-2-trifluormethylnaphthalene was obtained analogously. The needles had m.p. 131.5-132.5° (from aqueous alcohol).

Found %: N 4.08, 4.28; Cl 10.64. $C_{15}H_{11}O_2NF_3Cl$. Calculated %: N 4.25; Cl 10.75.

1-Acetylamino-2-trifluoromethylnaphthalene. A mixture of 1.47 g of 1-(N,N-diacetylamino)-2-trifluoromethylnaphthalene and 20 ml of 20% hydrochloric acid was boiled for 3 hr and cooled and the product collected and washed with water. The yield was 1.1 g (87%) and the needles had m. p. 192-194° (from aqueous alcohol).

Found %: N 5.50, 5.55; F 22.04, 22.26. $C_{13}H_{10}ONF_3$. Calculated %: N 5.52; F 22.50.

1-Acetylamino-4-chloro-2-trifluoromethylnaphthalene. Chlorine was passed for 30 min into a solution of 0.25 g of 1-acetylamino-2-trifluoromethylnaphthalene in 1.5 ml of glacial acetic acid at 100°. The mixture was cooled, diluted with water, and extracted with ether. The ether extract was washed with water, 2% sodium carbonate solution, and water and dried. The ether was removed in a water-pump vacuum and the residue recrystallized from aqueous alcohol and then from a mixture of ligroin and benzene. The yield was 0.17 g (60%) and the fine prisms had m. p. 198-199°.

Found %: N 4.91, 4.99; Cl 12.29. $C_{13}H_9ONF_3Cl$. Calculated %: N 4.90; Cl 12.33.

The product did not depress the melting point of the 1-acetylamino-4-chloro-2-trifluoromethylnaphthalene obtained by hydrolysis of the diacetyl derivative of (I) described above with 20% hydrochloric acid.

Hydrogenation of 1-chloro-2-trifluoromethylnaphthalene. A 1.4-g sample of 1-chloro-2-trifluoromethylnaphthalene was dissolved in 10 ml of methanol in the cold, 30 ml of 1 N potassium hydroxide in methanol and 6 g of moist Raney nickel (stored under a layer of alcohol) were added, and the mixture was hydrogenated at room temperature with mechanical shaking. The theoretical amount of hydrogen required for the replacement of all the halogen atoms was absorbed in 24 hr. The solution was filtered to remove the nickel and the residue on the filter washed with 30 ml of methanol. The alcohol was removed in a water-pump vacuum and the residue treated with water and ether. The ether extract was washed with water and dried. Removal of the ether yielded 0.65 g (75%) of an oil which crystallized slowly when stored for several days. The picrate, which had m. p. 115-117°, did not depress the melting point of the picrate obtained from an authentic sample of β-methylnaphthalene. Decomposition of the picrate with 20% sodium hydroxide yielded a crystalline substance with m. p. 35-36°, which did not depress the melting point of an authentic sample of β-methylnaphthalene.

α,β-(1,1,3,3-Tetrachloro)-naphthalane. The α,β-naphthalide used had m. p. 154-155°[6]. A mixture of 18.4 g of α,β-naphthalide, 70 g of phosphorus pentachloride, and 1 ml of phosphorus oxychloride was heated on an oil bath at 95-100° for 30 min and at 110-120° for 4 hr and at the end, the temperature was raised to 140°. Hydrogen chloride was liberated thereupon. During the reaction there distilled a mixture of phosphorus trichloride and phosphorus oxychloride, the residues of which were removed by heating in a water-pump vacuum on a water bath. The product distilled at 160-180°(0.1 mm). The yield was 18.5 g and the m. p. 112-118°. The product was dissolved in benzene and ammonia passed through the solution at room temperature for 1 hr. The solution was filtered to remove turbidity and evaporated to dryness. The yield was 18.0 g (58.5%) and the prisms had m. p. 122-123° (from ligroin).

Found %: Cl 45.78, 45.82. $C_{12}H_6OCl_4$. Calculated %: Cl 46.10.

Reaction of tetrachloronaphthalane with aniline. A solution of 0.52 g of tetrachloronaphthalane and 1.3 g of aniline in 6 ml of benzene was boiled for 5 hr. The solution was cooled and filtered to remove precipitated aniline hydrochloride, which was washed with benzene. The filtrate was evaporated to dryness and the residue treated with 20% hydrochloric acid and water and recrystallized from a mixture of benzene and ligroin. The yield was 0.18 g and the m. p. 213-214°.

Found %: N 8.12, 8.23. $C_{24}H_{16}ON_2$. Calculated %: N 8.05.

α,β-(1,1,3,3-Tetrafluoro)-naphthalane. a) A mixture of 3.1 g of α,β-(1,1,3,3-tetrachloro)-naphthalane and 6 g of antimony trifluoride was heated in a Claisen flask with a burner flame in a water-pump vacuum. The reaction product which distilled was treated with 20% hydrochloric acid and ether. The ether layer was washed with hydrochloric acid to remove antimony salts, water, sodium carbonate solution, and water and dried. The ether was removed and the residue recrystallized from ligroin. The yield was 1.1 g (45%) and the m. p. 54-55°.

Found %: F 31.05, 31.22. $C_{12}H_6OF_4$. Calculated %: F 31.40.

b) Into a polyethylene reactor, which was cooled with iced water and fitted with a copper reflux condenser with a water jacket, was placed 20.0 g of hydrogen fluoride and 9.24 g of tetrachloronaphthalane was introduced gradually in small portions. The ice bath was removed 20 min after the end of the addition and the reactor left at room temperature for 1 hr. The excess hydrogen fluoride was removed by distillation. The remaining product was treated with water and 1% potassium hydroxide solution, collected, washed with water, and dried. For the removal of impurity (the diacid fluoride of 1,2-naphthalenedicarboxylic acid), the product was dissolved in benzene and ammonia passed into the solution for 1 hr. The precipitate was collected, washed with benzene and water, and dried. It had m. p. 262-264° (with decomp.). When remelted, the same sample had m. p. 224-226°, which corresponds to the melting point of the diamide of 1,2-naphthalenedicarboxylic acid and its imide [9]. The benzene solution was evaporated to dryness in a water-pump vacuum. The yield of tetrafluoronaphthalane was 6.7 g (92%) and the m. p. 52-54°. The preparation did not depress the melting point of the tetrafluoronaphthalane described above.

When the unpurified tetrafluoronaphthalane was mixed with excess aniline in benzene, a product with m. p. 221° precipitated. It did not depress the melting point of the dianilide of 1,2-naphthalenedicarboxylic acid, which was obtained from the corresponding diacid chloride and aniline in benzene.

Found%: N 7.56, 7.65. $C_{24}H_{12}O_2N_2$. Calculated %: N 7.65.

Reaction of 2-trifluoromethyl-1-naphthoyl chloride (IX) with aluminum chloride. The acid chloride (IX) was obtained from 2-trifluoromethyl-1-naphthoic acid and phosphorus pentachloride. It had m. p. 44° (from ligroin). Boiling the acid chloride (IX) with a concentrated solution of aniline in benzene formed the anilide. The needles had m. p. 221° (from alcohol).

Found %: N 4.35, 4.38. $C_{18}H_{12}ONF_3$. Calculated %: N 4.45.

To a solution of 1.3 g of the acid chloride (IX) in 7 ml of anhydrous carbon disulfide was added 1.4 g of sublimed aluminum chloride with stirring and cooling. The mixture was boiled for 1 hr, the carbon disulfide removed in vacuum, and the residue decomposed with 25% hydrochloric acid with cooling to −10°. The product was extracted with benzene and the extract washed with 25% hydrochloric acid and water and dried. The benzene was removed and the residue recrystallized from ligroin. The purified product was dissolved in benzene and ammonia passed through the solution at room temperature for 1 hr. The solution was filtered free from turbidity and the benzene removed in a water-pump vacuum. The yield was 0.95 g (61%) and the m. p. 120-121°. The product did not depress the melting point of an authentic sample of tetrachloronaphthalane.

1,1,3,3-Tetrafluorophthalane. Into the polyethylene reactor described above, which was cooled with iced water, was placed 20 g of hydrogen fluoride and 7.75 g of tetrachlorophthalane added in small portions. The reaction began instantaneously and was accompanied by vigorous evolution of hydrogen chloride. The ice bath was removed 20 min after the end of the addition and the reactor left at room temperature for 1 hr. The excess hydrogen fluoride was removed by distillation. The residue was treated with water, extracted with ether, 1% potassium carbonate solution, and water, and dried. A stream of dry ammonia was passed into the ether solution for 20 min with cooling with ice. A mixture of the diamide of phthalic acid and ammonium fluoride precipitated. The precipitate was collected and washed with ether, which was added to the main filtrate, and water, and dried. The yield of the diamide of phthalic acid was 0.6 g and the m. p. 218-219°. The ether was removed from the filtrate in vacuum and the residue distilled with a short fractionating column. The yield of tetrafluorophthalane was 4.0 g (70%). It had b. p. 150-152° and n_D^{20} 1.4145.

SUMMARY

1. 1-Chloro- and 1,4-dichloro-2-trifluoromethylnaphthalenes were obtained from the corresponding trichloromethyl derivatives by means of anhydrous hydrofluoric acid.

2. 1-Amino-4-chloro-2-trifluoromethylnaphthalene, the naphthalene analog of the azo amine Brilliant ruby J, was snythesized.

3. α, β-(1,1,3,3-Tetrachloro)- and α, β-(1,1,3,3-tetrafluoro)-naphthalanes were prepared. It was shown that 2-trifluoromethyl-1-naphthoyl chloride gives α, β-(1,1,3,3-tetrachloro)-naphthalane on reaction with aluminum chloride.

4. It was found that in the fluorination of tetrachlorophthalane with anhydrous hydrogen fluoride in the cold there is no isomerization to o-trichloromethylbenzoyl chloride; only tetrafluorophthalane is formed.

5. Hydrogenation of 1-chloro-2-trifluoromethylnaphthalene in the presence of Raney nickel and excess alcoholic potassium hydroxide in the cold yielded 2-methylnaphthalene. There was unusual replacement of fluorine by hydrogen in a very stable trifluoromethyl group attached to an aromatic nucleus.

LITERATURE CITED

1. L. M. Yagupol'skii, Yu. A. Fialkov, ZhOKh 29, 3082 (1959).
2. R. Wolffenstein, Ber. 21, 1186 (1888).
3. K. Konig, Ber. 22, 787 (1889); 23, 806 (1890).
4. H. Kammerer, L. Horner, H. Beck, Ber. 91, 1376 (1958).
5. E. Ott, Ber. 55, 2108 (1922).
6. J. Hirschberg, D. Lavie, E. Bergmann, J. Chem. Soc. 1951, 1030.
7. L. M. Yagupol'skii, ZhOKh 30, 3444 (1960).
8. A. Reissert, Ber. 44, 866, 3061 (1911).
9. P. Cleve, Ber. 25, 2475 (1892).

INVESTIGATIONS OF BENZIMIDAZOLE DERIVATIVES

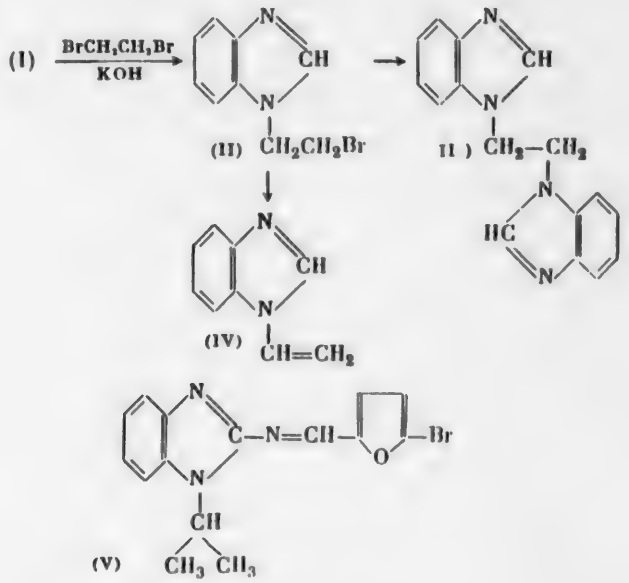
VIII. AMINATION OF SOME 1-SUBSTITUTED BENZIMIDAZOLES

A. M. Simonov and A. F. Pozharskii

Rostov-on-Don State Universtiy

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp 3970-3974, December, 1961
Original article submitted January 20, 1960

The amination of compounds of the benzimidazole series containing methyl, ethyl, γ-diethylaminopropyl, and benzyl groups in position 1 was studied previously [1]. Continuing this investigation, we treated 1-propyl-, 1-isopropyl-, and 1-n-butylbenzimidazole and also 1,2-di(N-benzimidazolyl)-ethane (III) with sodamide. The given compounds were obtained by the action of the appropriate alkyl halide on benzimidazole in alcohol in the presence of potassium hydroxide; from the reaction between benzimidazole (I) and 1,2-dibromoethane we also isolated 1-(β-bromoethyl)- (II) and 1-vinylbenzimidazole (IV).



The amination of the 1-alkylbenzimidazoles obtained proceeded readily in anhydrous xylene. 2-Amino-1-isopropylbenzimidazole was formed in a lower yield (40%) than the isomeric 2-amino-1-propylbenzimidazole (50%) and 2-amino-1-n-butylbenzimidazole (55%). The greater difficulty of the reaction with the isopropyl derivative is evidently caused by a certain increase in the electron density in the imidazole ring under the action of the positive induction effect of the isopropyl group, which is greater than that of the propyl and n-butyl groups (cf., for example, the basicity constants of 1-alkylbenzimidazoles [2]).

The yields of 2-amino derivatives of 1-isopropyl- and 1-propylbenzimidazoles when the reaction was carried out in dimethylaniline were lower than in xylene.

1,2-Di(N-benzimidazolyl)-ethane was not aminated in either solvents, evidently because of a steric effect. An examination of a Stuart model of the molecule shows that the hydrogen atoms in position 7 of the benzimidazole

nuclei prevent free rotation of the methylene groups. As a result of this and also as a result of the large volume of the benzimidazole nuclei, this disubstituted ethane can exist only in a completely inhibited conformation. In it the hydrogen atoms of the CH_2 groups screen positions 2 and 2' to a considerable extent and this naturally hinders the attack of sodium amide on these position.

According to the experiments of N. F. Vanieva in the Pharmacology Department of Rostov Medical Institute, 2-amino-2-isopropylbenzimidazole hydrochloride shows a hypotensive effect in tests on laboratory animals.

The 2-amino-1-alkylbenzimidazoles obtained were treated with 5-substituted furfurals; aldehydes whose derivatives have a strong physiological action in a number of cases were used [3]. The reaction with 5-halofurfurals proceeded readily in boiling alcohol. 5-Nitrofurfural reacted with 2-amino-1-isopropylbenzimidazole even in the cold and heating the reaction mixture led to tar formation as a result of the high basicity of the amine.

According to analysis data, the products were azomethynes such as (V) and not bisbenzimidazolylimino derivatives (cf. [4]).* When heated with dilute hydrochloric acid, the reaction products were hydrolyzed readily to form the starting materials.

EXPERIMENTAL

1-Isopropylbenzimidazole [2]. The colorless oil had b. p. 161-163° (10 mm). The picrate formed light yellow needles with m. p. 195-196° (from alcohol).

Found %: N 17.96. $C_{10}H_{12}N_2 \cdot C_6H_3O_7N_3$. Calculated %: N 17.99.

2-Amino-1-isopropylbenzimidazole. A mixture of sodium amide (from 2.0 g of sodium in liquid ammonia) and 10.1 g of 1-isopropylbenzimidazole was heated gradually with stirring in 50 ml of anhydrous xylene. The mixture was boiled for 3 hr. To the cooled reaction mixture was added sodium carbonate solution and the precipitate collected and washed with water and benzene. The very impure amination product was recrystallized from benzene. The yield was 4.4 g (39%) and this fell to 22-23% when the reaction was carried out in dimethylaniline. The compound formed colorless needles with m.p. 195-196° (from benzene), which dissolved when heated in water and in alcohol.

Found %: N 23.90, 24.08. $C_{10}H_{13}N_3$. Calculated %: N 23.98.

Picrate. The yellow needles had m. p. 251-252° (decomp., from alcohol).

Hydrochloride. The colorless needles (from alcohol and ether) were readily soluble in alcohol and water and insoluble in ether. They had m. p. 221-223°.

Found %: Cl 17.00. $C_{10}H_{13}N_3 \cdot HCl$. Calculated %: Cl 16.74.

2-(5'-Bromofurfurylidenamino)-1-isopropylbenzimidazole (V). An alcohol solution of equimolecular amounts of the 2-amino derivative and 5-bromofurfural was boiled for 1 hr. The alcohol was removed and the oily residue stirred with ether. The yield was 63%. The yellow crystals had m. p. 137° (from aqueous alcohol).

Found %: N 12.31, 12.32. $C_{15}H_{14}ON_3Br$. Calculated %: N 12.65.

2-(5'Nitrofurfurylidenamino)-1-isopropylbenzimidazole. A solution of the 2-amino derivative and 5'-nitrofurfural in alcohol was stirred at 20° for 3 hr. The yield was 40%. The fine orange needles had m. p. 197-198° (decomp., from alcohol).

Found %: N 18.71, 18.77. $C_{15}H_{14}O_3N_4$. Calculated %: N 18.78.

1-Propylbenzimidazole [2,6,7]. The colorless oil had b. p. 167-169° (10 mm) and crystallized slowly during storage. The m. p. was 30°.

Picrate. The light yellow crystals had m. p. 180-181° (from alcohol).

*The formation of pyrollal derivatives by furfural is observed only when it is treated with weakly basic amines in the presence of small amounts of mineral acid [5].

According to literature data: m. p. 204-206° [6], 180-181° [7]; 185° [2].

Found %: N 17.78, 18.02. $C_{10}H_{12}N_2 \cdot C_6H_3O_7N_3$. Calculated %: N 17.99.

2-Amino-1-propylbenzimidazole. This was obtained by amination of 1-propylbenzimidazole. The yield was 50%. The fine needles had m. p. 132-133° (from benzene) and were soluble in alcohol and water on heating and insoluble in ether.

Found %: N 24.29. $C_{10}H_{13}N_3$. Calculated %: N 23.98.

2-(5'-Chlorofurfurylidenamino)-1-propylbenzimidazole. The yellow crystals had m. p. 106-107° (from aqueous alcohol) and were soluble in acetone. The yield was 60%.

Found %: N 14.91. $C_{15}H_{14}ON_3Cl$. Calculated %: N 14.61.

1-Butylbenzimidazole. The yellowish oil gradually became red on standing. It had b. p. 171-173° (5 mm).

Found %: N 15.95. $C_{11}H_{14}N_2$. Calculated %: N 16.08.

Picrate. The yellow crystals (from alcohol) had m. p. 162.5-163°.

Found%: N 17.15. $C_{11}H_{14}N_2 \cdot C_6H_3O_7N3$. Calculated %: N 17.36.

2-Amino-1-n-butylbenzimidazole. This was obtained by the action of sodium amide on 1-n-butylbenzimidazole in xylene. The yield was 55%. The snow white needles (from benzene) had m. p. 127-128° and were soluble in alcohol and hot water.

Found %: N 22.42, 22.09. $C_{11}H_{15}N_3$. Calculated %: N 22.20.

2-(p-Nitrobenzylidenamino)-1-n-butylbenzimidazole. The yellow needles had m.p. 154-155° (from alcohol).

Found %: N 17.31. $C_{18}H_{18}O_2N_4$. Calculated %: N 17.38.

1,2-Di(N-benzimidazolyl)-ethane (III). A solution of 18.9 g of benzimidazole. 30 g of 1,2-dibromoethane, and 13.4 g of 80% potassium hydroxide in 70 ml of alcohol was boiled for 2.5 hr and filtered to remove the potassium bromide and the alcohol distilled from the filtrate. The resdiue (a mixture of crystals and oil) was treated with water (50 ml) and filtered. The filtrate separated into two layers. From the lower, oily layer we isolated the bis derivative (0.4 g) and β-bromoethylbenzimidazole (1 g). The residue on the filter, which contained unreacted benzimidazole (10-11 g), was treated with chloroform (70 ml) and the chloroform extract washed carefully with 10% sodium hydroxide solution and then water. The residue after removal of the chloroform was treated with ether. From the ether extract we isolated an oil (0.8 g), which decolorized bromine water and a solution of potassium permanganate and consisted of 1-vinylbenzimidazole (IV). The picrate formed yellow crystals with m. p. 193-194°. According to literature data: m. p. 194-195° [8].

The ether-insoluble portion of the crystals was 1,2-di(N-benzimidazolyl)-ethane. The yield was 2.4-3.4 g (11.3-16.2%). The colorless tablets or prisms had m. p. 225-226° (from water or xylene).

Found %: N 21.51, 21.69. $C_{16}H_{14}N_4$. Calculated %: N 21.37.

The use of excess dibromoethane led, in addition, to the formation of a crystalline product, which contained ionic bromine (about 28%) and was a mixture of quaternary salts.

When 1,2-di(N-benzimidazolyl)-ethane was heated (140°, 3 hr) with sodium amide (30% excess) there was no liberation of hydrogen or a change in the color of the reaction mixture (a characteristic sign of amination). The starting base was recovered in 82% yield (95% in dimethylaniline).

The dipicrate of 1,2-di(N-benzimidazolyl)-ethane was formed by mixing alcohol solutions of the bis derivative and picric acid (2 moles). The yield was quantitative. The yellow crystals darkened gradually when heated above 220° and melted with decomposition at 292-293°.

Found %: N 19.63. $C_{16}H_{14}N_4 \cdot 2C_6H_3O_7N_3$. Calculated %: N 19.44.

Bisiodomethylate. This was formed by boiling a solution of the bis derivative with excess methyl iodide in methanol. The slighly yellowish needles (from water or aqueous alcohol) darkened when heated above 220° and melted with decomposition at 269°.

Found %: I 46.25, 46.33, $C_{18}H_{20}N_4I_2$. Calculated %: I 46.46.

1-(β-Bromoethyl)-benzimidazole (II). This was a very viscous, light yellow oil, which dissolved readily in ether. On prolonged standing, it changed into a solid, ether-insoluble, polymeric, amorphous product.

Found %: N 12.14, 12.17. $C_9H_9N_2Br$. Calculated %: N 12.45.

Picrate. The yellow crystals had m. p. 169° (decomp., from alcohol).

SUMMARY

1. 1-Propyl-, 1-isopropyl-, and 1-n-butylbenzimidazoles were subjected to direct amination. The 2-amino-1-alkylbenzimidazoles obtained formed azomethynes when treated with 5-halo- and 5-nitrofurfurals.

2. We synthesized 1,2-di(N-benzimidazolyl)-ethane, which could not be aminated.

LITERATURE CITED

1. A. M. Simonov, P. A. Uglov, ZhOKh 21, 884 (1951); N. D. Vitkevich, A. M. Simonov, ZhOKh 29, 2614 (1959); A. M. Simonov, N. D. Vitkevich, ZhOKh 30, 590 (1960); A. M. Simonov, N. D. Vitkevich, B. K. Martsokha, ZhOKh 30, 3062 (1960).
2. M. Davies, P. Mamelis, V. Petrov, B. Sturgeon, J. Pharm. Pharmacol 3, 420 (1951).
3. S. A. Giller, Furacillin [in Russian] Izd. AN Latv. SSR (1953); Z. N. Nazarova, T. V. Ustimenko, ZhOKh 30, 2017 (1960).
4. R. W. Drisko, H. McKennis, J. Am. Chem. Soc. 74, 2626 (1952).
5. A. P. Terent'ev, L. A. Yanovskaya, Usp. khim. 23, 728 (1954); Synth. Org. Prep. [Russian translation] I, 120 (1950).
6. K. Auwers, W. Mauss, Ber. 61, 2411 (1928).
7. R. Weidenhagen, G. Train, H. Wegner, L. Nordstrom, Ber. 75, 1936 (1942).
8. J. Meisenheimer, B. Wieger, J. pr. Ch. 102, 45 (1921).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

β-DICARBONYL COMPOUNDS

XIV. SYNTHESIS, CONVERSIONS, AND BIOLOGICAL ACTIVITY OF DERIVATIVES OF 2-(3'-METHYL-2'-BUTENYL)-DIHYDRORESORCINOL

V. I. Gunar, S. I. Zav'yalov, G. N. Pershin,

S. N. Milovanova, N. S. Bogdanova, O. O. Makeeva,

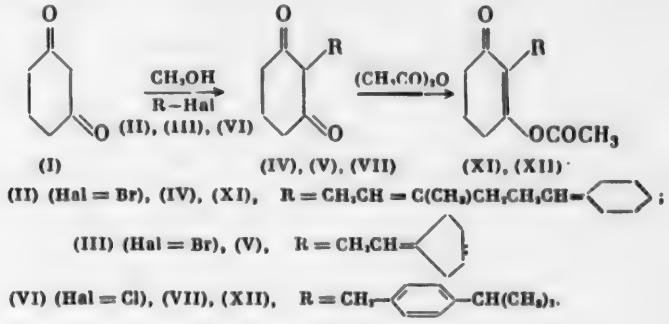
and A. I. Krotov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR, S. Ordzhonikidze All-Union Chemicopharmaceutical Scientific Research Institute, and Institute of Malaria, Medical Parasitology, and Helminthology

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 3975-3984, December, 1961
Original article submitted December 12, 1960

In a continuation of previous work [1, 2] on the synthesis of physiologically active derivatives of dihydroresorcinol, we prepared a series of new 2-(3'-methyl-2'-butenyl)-dihydroresorcinols and converted them into acids and polycyclic compounds. Some of the substances synthesized were tested for bacteriostatic, fungistatic, antiviral, and anthelminthic action.

The alkylation of dihydroresorcinol (I) in methanol with allyl bromides (II, III), prepared from 6-cyclohexylidene-3-methylhexen-1-ol-3 and 1-vinyl-cyclopentanol-1, formed 2-(6'-cyclohexylidene-3'-methylhexen-2'-yl)- (IV) and 2-(2'-cyclopentylidenethyl)-dihydroresorcinols (V).



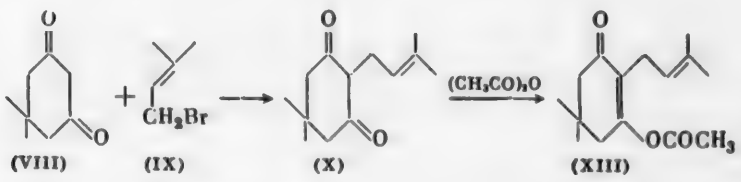
(I) (IV), (V), (VII) (XI), (XII)

(II) (Hal = Br), (IV), (XI), R = $CH_2CH=C(CH_3)CH_2CH_2CH=$;

(III) (Hal = Br), (V), R = $CH_2CH=$;

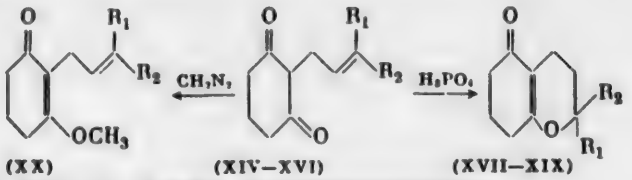
(VI) (Hal = Cl), (VII), (XII), R = CH_2- $-CH(CH_3)_2$.

For comparison of the physiological properties, 2-(p-isopropylbenzyl)-dihydroresorcinol (VII) was prepared analogously from dihydroresorcinol (I) and p-isopropylbenzyl chloride (VI) and 2-(3'-methyl-2'-butenyl)-dimedone (X) from dimedone (VIII) and 3-methyl-2-butenyl bromide (IX).



(VIII) (IX) (X) (XIII)

For the same purpose, the β-diketones (XIV-XVI), which have been described previously [1], were converted into the chromanones (XVII-XIX) [the methyl ether (XX) was obtained from the β-diketone (XIV)] and the newly prepared diketones (IV, VII, and X) were converted into the enol acetates (XI-XIII).

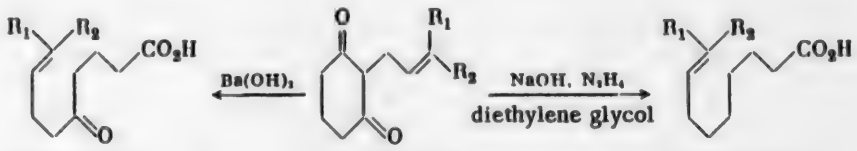


(XX) (XIV–XVI) (XVII–XIX)

(XIV, XVII, XX) $R_1 = CH_3$, $R_2 = CH_2CH_2CH_2CH(CH_3)_2$;
(XV, XVIII) $R_1 = CH_3$, $R_2 = CH_2CH_2CH{=}C(CH_3)_2$;
(XVI, XIX) $R_1 = CH_3$, $R_2 = CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$.

In connection with the interesting biological properties of higher branched acids, such as the stimulating action on the healing of wounds of α-cyclohexyl- and α-hexylgeronylacetic acids [3], the antibacterial action of 3,7,11-trimethyldodecatetraen-2,4,6,10-oic and ionolideneacetic acids [4], and the antileprous effect of chaulmoogric and hydnocarpic acids, it seemed profitable to cleave the β-diketones (V, XIV-XVI) by the methods of Vorländer [5] and Stätter [6] and prepare analogs of the above compounds.

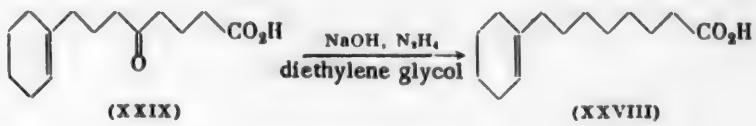
Hydrolytic cleavage of the β-diketones(V, XIV, and XVI) with barium hydroxide made it possible to obtain the δ-keto acids (XXI, XXII, and XXIII). Reductive cleavage [6] of the β-diketones (V and XIV-XVI) by Stätter's method led to the unsaturated branched acids (XXIV-XXVII), including the structural analog of chaulmoogric acid (XXVII).



(XXI–XXIII) (V, XIV–XVI) (XXIV–XXVII)

(XIV, XXI, XXIV) $R_1 = CH_3$, $R_2 = CH_2CH_2CH_2CH(CH_3)_2$;
(XV, XXV) $R_1 = CH_3$, $R_2 = CH_2CH_2CH{=}C(CH_3)_2$;
(XVI, XXII, XXVI) $R_1 = CH_3$, $R_2 = CH_2CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$;
(V, XXIII, XXVII) R_1, $R_2 = CH_2CH_2CH_2CH_2$.

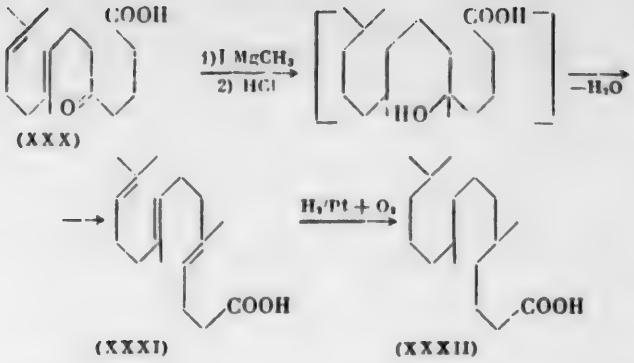
We obtained the analog of chaulmoogric acid containing a six-membered ring (XXVIII) by a Kizhner reduction of 5-keto-8-(1'-cyclohexenyl)-octanoic acid (XXIX), whose synthesis was described previously [7].



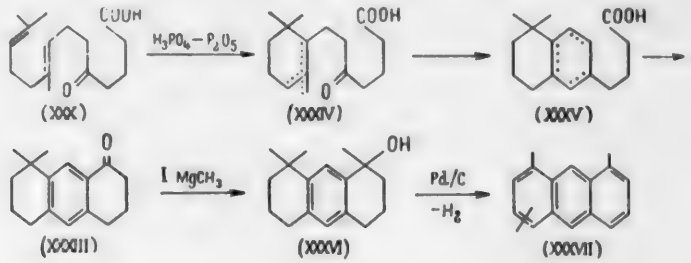
(XXIX) (XXVIII)

We previously put forward a method of synthesizing isoprenoid acids and polycyclic compounds from δ-keto acids [8]. Analogous conversions were achieved in the present work on a new example.

Treatment of the potassium salt of 5-keto-9,13-dimethyltetradecadien-8,12-oic acid [9] (XXX) with excess methyl magnesium iodide yielded farnesylacetic acid (XXXI). Hydrogenation of this over platinum oxide with the absorption of 3 equivs. of hydrogen led to hexahydrofarnesylacetic acid (XXXII).



Heating 5-keto-9,13-dimethyltetradecadien-8,12-oic acid (XXX) with polyphosphoric acid for 3 hr at 100° yielded 1-keto-8,8-dimethyl-1,2,3,4,5,6,7,8-octahydroanthracene (XXXIII) as a result of a triple cyclization.



The above conversion of the unsaturated keto acid (XXX) into the ketone (XXXIII) evidently proceeds through several stages, including the formation of the monocyclic keto acid (XXXIV), analogous to the cyclization of 1,5-dienes in the terpene series [10], and the bicyclic acid (XXXV) with subsequent aromatization and intramolecular acylation. The last reaction evidently should lead only to an anthracene derivative as there are data on the difficulty of intramolecular acylation in the ortho-position relative to a substituent present in the ring [11].

The structure of the anthracene derivative obtained (XXXIII) agrees with elementary analysis data on the ketone itself and its 2,4-dinitrophenylhydrazone (λ_{max} 389 mμ in alcohol). The action of methylmagnesium iodide on the ketone (XXXIII) and dehydrogenation of the alcohol thus formed (XXXVI) with Pd/C yielded a mixture of methyl-substituted anthracenes (XXXVII) with m. p. 123-130° which could not be separated even by chromatography. An analogous picture is observed in the dehydrogenation of other gem-substituted cyclic systems [12].

The anthracene structure of the dehydrogenation products (XXXVII) and, consequently, the structure of the ketone (XXXIII) itself was confirmed by comparison of its ultraviolet spectrum with the spectra of methyl-substituted anthracenes [13] and phenanthrenes [14]. The absorption intensity of the K-band of anthracene derivatives at 257mμ is considerably higher than that of the corresponding phenanthrene compounds. In addition, the latter show no absorption at all in the region of 360-400 mμ, which is present in the spectrum of anthracenes. These data make it possible to distinguish very clearly between the two series of substances mentioned.

The keto acid (XXIX), which has been described previously, and also some of the newly prepared derivatives of dihydroresorcinol (IV, VII, X, XI, XII, XIII, XVII, XX) were tested for bacteriostatic, fungistatic, antiviral, and anthelminthic action in vitro (see table).

The preparations (VII, XII, X, XIII, XXIX) were tested against acid-fast bacteria and fungi beginning with a dilution of 1:1000 and against other bacteria beginning with a dilution of 1:2000, while the preparations (IV, XI, XVII, XX) were tested beginning with dilutions of 1:200 and 1:400, respectively.

The chromanones (XIX and XVII) and the methyl ether (XX) showed tuberculostatic activity in cultures of tuberculosis bacteria (human type, strain Academia) at dilutions of 1:4,000,000, 1:1,000,000 and 1:10,000,000 and against the strain H37PV with horse serum at dilutions of 1:16,000, 1:64,000 and 1:32,000. In experiments on animals (experimental tuberculosis of white mice), the preparation (XX) was found to be inactive.

Biological Activity of Compounds *

Compound No. / Type of test	Staphylococcus aureus	Streptococcus hemolyticus	Bacillus coli	Typhoid bacillus	Flexner's bacillus	Diphtherial bacillus strain PW$_8$	Bacillus pyocyaneus	Proteus vulgaris	Anthrax spores	Human tuber. bacillus (deep culture)	Avian tuber bacillus	Acid-fast saprophyte B$_8$	Microsporon	Trichophyton	Achorion	Actinomyces	Yeast-like fungi	Antiviral activity	Anthelmintic activity
(IV)	0	0	0	0	1 : 4000	0	0	0	0	1 : 125000	1 : 60000	1 : 60000	0	0	0	1 : 1000	0	0	+
(XI)	1 : 400	1 : 400	0	0	1 : 1600	0	0	0	0	1 : 125000	1 : 25000	1 : 12000	1 : 200	0	1 : 200	0	0	0	+
(VII)	1 : 2000	1 : 2000	0	0	1 : 2000	1 : 2000	0	0	1 : 2000	0	0	0	1 : 4000	1 : 2000	1 : 4000	0	0	0	0
(XII)	0	0	0	0	0	0	0	0	0	1 : 2000	1 : 2000	1 : 2000	1 : 4000	1 : 4000	1 : 4000	1 : 2000	0	0	0
(X)	0	0	0	0	0	0	0	0	0	0	1 : 1000	1 : 100	0	0	0	0	0	0	0
(XIII)	1 : 400	1 : 400	0	0	1 : 400	1 : 400	0	0	1 : 400	1 : 1600	1 : 3000	1 : 800	1 : 800	1 : 400	1 : 400	1 : 25000	1 : 200	0	0
(XVII)	1 : 6000	1 : 3000	0	0	1 : 6000	1 : 6000	0	0	1 : 6000	1 : 1000000	1 : 125000	1 : 25000	1 : 12500	1 : 6000	1 : 12500	1 : 25000	0	0	0
(XX)	1 : 6000	1 : 6000	0	0	1 : 6000	1 : 6000	0	0	1 : 6000	1 : 1000000	1 : 25000	1 : 25000	1 : 6000	1 : 6000	1 : 12000	1 : 25000	1 : 2000	0	0
(XXIX)	0	0	0	0	0	0	0	0	0	1 : 4000	1 : 2000	1 : 2000	1 : 2000	1 : 1000	1 : 2000	1 : 1000	1 : 2000	0	0

*The preparations were tested at dilutions of 1:1000 against 1 lethal dose of influenza virus. The tests for bacteriostatic and fungistatic action (suppression of the growth of microorganisms) began with a dilution of 1:200.

The acids (XXII, XXVI, XXIV) and the chromanone (XVIII) neutralized one fatal dose of influenza virus in dilutions of 1:100,000, 1:300,000, 1:30,000, and 1:1000, respectively.

Only the β-diketone (IV) and the enol acetates (XI and XII) showed anthelminthic activity against Ascaris in vitro.

EXPERIMENTAL

2-(6'-Cyclohexylidene-3'-methylhexen-2'-yl)-dihydroresorcinol (IV). The bromide (II) was prepared from 188 g of 6-cyclohexylidene-3-methylhexen-1-ol-3 [15] by the usual method with anhydrous gaseous hydrogen bromide. Without further purification, the bromide (II) was added at −10° to a solution of the sodium derivative of dihydroresorcinol prepared from 22.5 g of sodium, 500 ml of methanol, and 112 g of dihydroresorcinol. When all the bromide had been added, the temperature was slowly raised to room temperature and then the mixture boiled for 3 hr. After removal of the methanol in vacuum, the residue was treated with 3% sodium hydroxide solution and the alkaline layer extracted with ether, cooled, and acidified to Congo with hydrochloric acid. The precipitate was collected and dried at room temperature. We obtained 100 g of 2-(6'cyclohexylidene-3'-methylhexen-2'-yl)-dihydroresorcinol (IV) with m. p. 112-113° (from 80% methanol). The yield was 35%, calculated on the starting carbinol.

Found %: C 79.00, 78.90; H 9.72, 9.71. $C_{19}H_{28}O_2$. Calculated %: C 79.12; H 9.79.

Enol acetate of 2-(6'-cyclohexylidene-3'-methylhexen-2'-yl)-dihydroresorcinol (XI). A mixture of 17.6 g of the diketone (IV) and 100 ml of acetic anhydride was boiled for 3 hr. Distillation yielded 17.2 g of the enol acetate (XI) with b. p. 180-183° at 0.5 mm and n_D^{20} 1.5173. The yield was 86%.

Found %: C 75.90, 76.01; H 9.13, 9.25. $C_{21}H_{30}O_3$. Calculated %: C 76.32; H 9.15.

The 2,4-dinitrophenylhydrazone had m. p. 88.5-89.5° (from a mixture of methanol and dioxane).

Found%: N 10.82, 10.63. $C_{27}H_{34}O_6N_4$. Calculated %: N 10.97.

2-(2'-Cyclopentylidenethyl)-dihydroresorcinol (V). Treatment of 61 g of 1-vinylcyclopentanol-1 with gaseous hydrogen bromide yielded the bromide (III), which, without further purification, was added at room temperature to a solution of the potassium derivative of dihydroresorcinol, which had been prepared from 30.8 g of potassium hydroxide, 200 ml of methanol,

and 62 g of dihydroresorcinol. Boiling for 3 hr and the usual treatment yielded 83 g of 2-(2'-cyclopentylidenethyl)-dihydroresorcinol (V) with m. p. 151-152° (from 60% methanol). The yield was 72%, calculated on the starting carbinol.

Found %: C 75.55, 75.80; H 8.85, 8.84. $C_{13}H_{18}O_2$. Calculated %: C 75.69; H 8.80.

2-(p-Isopropylbenzyl)-dihydroresorcinol (VII). At room temperature, 84.5 g of p-isopropylbenzyl chloride (VI) was added to a solution of the sodium derivative of dihydroresorcinol, which was prepared from 11.5 g of sodium, 500 ml of methanol, and 60 g of dihydroresorcinol. Boiling for 4 hr and the usual treatment gave 73 g of 2-(p-isopropylbenzyl)-dihydroresorcinol (VII) with m. p. 168-170° (from 50% methanol). The yield was 60%. The product was unstable and decomposed when stored at room temperature for 2 days.

Found %: C 78.94, 78.82; H 8.29, 8.24. $C_{16}H_{20}O_2$. Calculated %: C 78.65; H 8.25.

Enol acetate of 2-(p-isopropylbenzyl)-dihydroresorcinol (XII). Boiling a mixture of 12 g of the diketone (VII) and 60 ml of acetic anhydride yielded 12.8 g of the enol acetate (XII) with b. p. 160-164° at 0.5 mm and m. p. 50-51° (from heptane). The yield was 91.5%.

Found %: C 75.02, 75.08, H 7.58, 7.59. $C_{18}H_{22}O_3$. Calculated %: C 75.49; H 7.74.

2-(3'-Methyl-2'-butenyl)-dimedone (X). To a solution of the sodium derivative of dimedone, prepared from 3.8 g of sodium, 200 ml of methanol, and 23 g of dimedone (VIII), was added 29 g of 3-methyl-2-butenyl bromide (IX) at 4-10° and then the temperature was slowly raised to room temperature and the mixture boiled and stirred for 4 hr. After removal of the solvent, the residue was treated with 3% sodium hydroxide solution, the alkaline layer extracted with ether, cooled, and acidified to Congo with hydrochloric acid and the precipitate collected, washed with hot water to remove dimedone, and dried at room temperature. We obtained 18.5 g of 2-(3'-methyl-2'-butenyl)-dimedone (X) with m. p. 119-121° (from 50% methanol). The yield was 45%.

Found %: C 75.02, 75.17; H 9.55, 9.73. $C_{13}H_{20}O_2$. Calculated %: C 74.96; H 9.68.

Enol acetate of 2-(3'-methyl-2'-butenyl)dimedone (XIII). Boiling a mixture of 10 g of 2-(3'-methyl-2'-butenyl)dimedone (X) and 50 ml of acetic anhydride for 3 hr yielded 11.3 g of the enol acetate (XIII) with b. p. 105-109° at 0.5 mm and n_D^{20} 1.4880.

Found %: C 71.78, 71.72; H 8.61, 8.54. $C_{15}H_{22}O_3$. Calculated %: C 71.97; H 8.86.

The 2,4-dinitrophenylhydrazone of compound (XIII) could not be obtained.

2-Methyl(-2-isohexyl-5,7-tetrahydrochromanone-5 (XVII). A mixture of 10 g of 2-(3',7'-dimethylocten-2'-yl)-dihydroresorcinol (XIV) was heated with 40 g of crystalline phosphoric acid at 100° for 18 hr. The cooled reaction mixture was treated with water and extracted with ether and the extract washed with saturated sodium carbonate solution and water and dried with magnesium sulfate. Vacuum distillation yielded 7.8 g of the tetrahydrochromanone (XVII) with b. p. 124-125° at 0.5 mm and n_D^{20} 1.5032. The yield was 73%.

Found %: C 76.85, 76.65; H 10.45, 10.43. $C_{16}H_{26}O_2$. Calculated %: C 76.75; H 10.45.

The 2,4-dinitrophenylhydrazone had m. p. 154-155° (from a mixture of methanol and dioxane) and λ_{max} 406 mμ (in alcohol).

Found %: N 13.41, 13.26. $C_{22}H_{30}O_5N_4$. Calculated %: N 13.02.

2-Methyl-2-(4'-methylpenten-3'-yl)-5,7-tetrahydrochromanone-5 (XVIII). Heating a mixture of 30 g of 2-(3',7'-dimethyloctadien-2',6',-yl-dihydroresorcinol (XV) and 200 g of crystalline phosphoric acid at 100° for 14 hr yielded 9.2 g of the tetrahydrochromanone (XVIII) with b. p. 138-142° at 0.5 mm and n_D^{20} 1.5330. The yield was 30%.

Found %: C 76.88, 76.89; H 9.74, 9.69. $C_{16}H_{24}O_2$. Calculated %: C 77.37; H 9.74.

The 2,4-dinitrophenylhydrazone of compound (XVIII) could not be obtained.

2-Methyl-2-(4',8'-dimethylnonyl)-5,7-tetrahydrochromanone-5 (XIX). Heating a mixture of 26.0 g of 2-(3',7',-11'-trimethyldodecen-2'-yl)-dihydroresorcinol (XVI) and 150 g of crystalline phosphoric acid at 100° for 6 hr yielded 18.0 g of the tetrahydrochromanone (XIX) with b. p. 166-170° at 0.4 mm and n_D^{20} 1.4922. The yield was 70%.

Found %: C 78.64, 78.65; H 11.47, 11.45. $C_{21}H_{36}O_2$. Calculated %: C 78.69; H 11.32.

The 2,4-dinitrophenylhydrazone had m. p. 105.5-106.5° (from a mixture of methanol and dioxane) and λ_{max} 401 mμ (in alcohol).

Found %: N 11.11, 11.06. $C_{27}H_{40}O_8N_4$. Calculated %: N 11.19.

Methyl ether of 2-(3',7'-dimethylocten-2'-yl)-dihydroresorcinol (XX). To an ether solution of diazomethane, prepared from 13.8 g of nitrosomethylurea, was added 15 g of 2-(3',7'-dimethylocten-2'-yl)-dihydroresorcinol (XIV) and the mixture left at room temperature for 12 hr. After removal of the solvent, the residue was vacuum distilled. We obtained 10.6 g of the methyl ether of the diketone (XX) with b. p. 149-154° at 0.5 mm and n_D^{20} 1.5100. The yield was 67%.

Found %: C 76.97, 77.01; H 10.81, 10.66. $C_{17}H_{28}O_2$. Calculated %: C 77.22; H 10.67.

The 2,4-dinitrophenylhydrazone of compound(XX) could not be obtained.

9,13-Dimethyltetradecen-8-oic acid (XXIV). An 8-g portion of powdered sodium hydroxide was dissolved in 60 ml of diethylene glycol with heating and then there were added 10 g of 2-(3',7'-dimethylocten-2'-yl)-dihydroresorcinol (XIV), 5 ml of 85% hydrazine hydrate, and sufficient methanol for the reaction mixture to boil at 125°. The mixture was boiled at this temperature for 35 hr and then the boiling point was raised to 195° by distillation of the volatile substances (methanol, water, and hydrazine hydrate) and heating continued for a further 13 hr. The cooled reaction mixture was diluted with water and acidified to Congo with hydrochloric acid and the liberated oil extracted with ether. The extract was washed with water and dried with magnesium sulfate, the ether removed, and the residue vacuum distilled. We obtained 6.0 g of 8,13-dimethyltetradecen-8-oic acid (XXIV) with b. p. 143-145° at 0.5 mm and $n_D^{21.5}$ 1.4590. The yield was 55%.

Found %: C 75.39, 75.67; H 11.70, 11.91. $C_{16}H_{30}O_2$. Calculated %: C 75.53; H 11.89.

The S-benzylthiouronium salt had m. p. 134.5-135.5° (from 50% methanol).

Found %: N 6.77, 6.98. $C_{24}H_{40}O_2N_2S$. Calculated %: N 6.66.

9,13-Dimethyltetradecadien-8,12-oic acid (XXV). Boiling a mixture of 13 g of powdered sodium hydroxide, 100 ml of diethylene glycol, 16 g of 2-(3',7'-dimethyloctadiene-2',6'-yl)-dihydroresorcinol (XV), and 8.1 ml of 85% hydrazine hydrate for 30 hr at 125° and 12 hr at 195° yielded 11.8 g of 9,13-dimethyltetradecadien-8,12-oic acid (XXV) with b. p. 153-155° at 0.5 mm and n_D^{20} 1.4728. The yield was 71%.

Found %: C 75.98, 76.24; H 11.12, 11.01. $C_{16}H_{28}O_2$. Calculated %: C 76.14; H 11.18.

The S-benzylthiouronium salt had m. p. 129-130° (from 50% methanol).

Found %: N 6.98, 6.71. $C_{24}H_{38}O_2N_2S$. Calculated %: N 6.69.

9,13,17-Trimethyloctadecen-8-oic acid (XXVI). As described above, from 21.2 g of 2-(3',7',11'-trimethyldodecen-2'-yl)-dihydroresorcinol (XVI), 13.2 g of powdered sodium hydroxide, and 8.3 ml of 85% hydrazine hydrate in 100 ml of diethylene glycol we obtained 14.1 of 9,13,17-trimethyloctadecen-8-oic acid (XXVI) with b. p. 180-182° at 0.35 mm and n_D^{20} 1.4618. The yield was 66%.

Found %: C 77.88, 77.65; H 12.50, 12.16. $C_{21}H_{40}O_2$. Calculated %: C 77.72; H 12.42.

The S benzylthiouronium salt had m. p. 129-130° (from 50% methanol).

Found %: N 5.59, 5.39. $C_{29}H_{50}O_2N_2S$. Calculated %: N 5.71.

8-Cyclopentylidenoctanoic acid (XXVII). Boiling a mixture of 51.6 g of 2-(2'-cyclopentylidenethyl)-dihydroresorcinol (V), 50 g of powdered sodium hydroxide, and 31.2 ml of 85% hydrazine hydrate in 375 ml of diethylene glycol yielded 28.1 g of 8-cyclopentylidenoctanoic acid (XXVII) with b. p. 135-137° at 0.4 mm, n_D^{20} 1.4765, and m. p. 21.5-22° (from heptane).

Found %: C 74.27, 74.08; H 10.50, 10.48. $C_{13}H_{22}O_2$. Calculated %: C 74.24; H 10.54.

8-(1'-Cyclohexenyl)-octanoic acid (XXVIII). In 70 ml of diethylene glycol was dissolved 4 g of powdered sodium hydroxide with heating and then 10.7 g of 5-keto-8-(1'-cyclohexenyl)-octanoic acid (XXIX) (b. p. 173° at 0.5 mm and n_D^{20} 1.4925 [7]) and 7 ml of 85% hydrazine hydrate were added. The reaction mixture was boiled

at 125° for 30 hr and then at 195° for 12 hr after distillation of the volatile substances. Normal treatment yielded 6.7 g of 8-(1'-cyclohexenyl)-octanoic acid (XXVIII) with b. p. 151-153° at 0.5 mm and n_D^{20} 1.4808. The yield was 67%.

Found %: C 75.11, 74.92; H 10.80, 10.60. $C_{14}H_{24}O_2$. Calculated %: 74.95; H 10.78.

The S-benzylthiouronium salt had m. p. 135-136° (from ethyl acetate).

Found %: N 7.23, 7.30. $C_{22}H_{34}O_2N_2S$. Calculated %: N 7.17.

5-Keto-9,13-dimethyltetradecen-8-oic acid (XXI). To a solution of 30 g of barium hydroxide in 180 ml of water was added 10 g of 2-(3'-7'-dimethyloctenyl-2')-dihydroresorcinol (XIV) and the mixture boiled for 24 hr. The cooled reaction mixture was acidified to Congo with hydrochloric acid and the liberated oil extracted with ether. We obtained 8.2 g of the keto acid (XXI) with b. p. 168-170° at 0.5 mm and n_D^{20} 1.4678. The yield was 76%.

Found %: C 71.70, 71.57; H 10.72, 10.76. $C_{16}H_{28}O_3$. Calculated %: C 71.60; H 10.52.

The S-benzylthiouronium salt had m. p. 133-134° (from 50% methanol).

Found %: N 6.45, 6.47. $C_{24}H_{38}O_3N_2S$. Calculated %: N 6.45.

5-Keto-9,13,17-trimethyloctadecen-8-oic acid (XXII). As described above, from 15 g of 2-(3',7',11'-trimethyldodecen-2'-yl)-dihydroresorcinol (XVI), 63 g of barium hydroxide, and 150 ml of water we obtained 11.7 g of the keto acid (XXII) with b. p. 205-207° at 0.5 mm and n_D^{20} 1.4690. The yield was 73%.

Found %: C 74.77, 74.50; H 11.33, 11.32. $C_{21}H_{38}O_3$. Calculated %: C 74.51; H 11.32.

The S-benzylthiouronium salt of compound (XXII) could not be prepared.

5-Keto-8-cyclopentylidenoctanoic acid (XXIII). Boiling a mixture of 41.2 g of 2-(2'-cyclopentylidenethyl)-dihydroresorcinol (V) and 252 g of barium hydroxide in 580 ml of water yielded 22 g of the keto acid (XXIII) with b.p. 173-175° at 0.5 mm and m.p. 45.5-46.5° (from heptane).

Found %: C 69.63; 69.43; H 8.82, 8.80. $C_{13}H_{20}O_3$. Calculated %: C 69.61; H 8.99.

Farnesylacetic acid (XXXI). To a suspension in 150 ml of absolute ether of the potassium salt obtained from 8.8 g of 5-keto-9,13-dimethyltetradecadien-8,12-oic acid [9] (XXX) and 1.85 g of potassium hydroxide was added a solution of methylmagnesium iodide (1.61 g of magnesium, 9.4 g of methyl iodide, and 50 ml of absolute ether) at −15°. After being stirred at −15° for 3 hr, the reaction mixture was left overnight and then treated with ice and dilute hydrochloric acid (1:1). The ether extract was washed with water, sodium hyposulfite solution, and again with water and dried with magnesium sulfate. After removal of the solvent, the residue was vacuum distilled. We obtained 6.1 g (61% yield) of farnesylacetic acid (XXXI) with b. p. 168-172° at 0.5 mm and n_D^{20} 1.4888.

Found %: C 77.22, 77.12; H 10.84, 10.65. $C_{17}H_{28}O_2$. Calculated %: C 77.22; H 10.67.

The S-benzylthiouronium salt was unstable and had m. p. 115-117° (from ethyl acetate).

The following constants are given in the literature for farnesylacetic acid: b. p. 154-155° (0.15 mm), n_D^{20} 1.4870, b. p. 155-160° (0.3 mm) and n_D^{25} 1.4865; S-benzylthiouronium salt: m. p. 116-117°, unstable, gives a poor analysis [16].

Hexahydrofarnesylacetic acid (XXXII). When 10.4 g of farnesylacetic acid (XXXI) was hydrogenated over platinum oxide in methanol, 2.45 liter of hydrogen was absorbed (calculated amount 2.6 liter). Distillation yielded 9.2 g of hexahydrofarnesylacetic acid with b. p. 138-139° at 0.5 mm and n_D^{20} 1.4520.

Found %: C 75.55, 75.40; H 12.40, 12.40. $C_{13}H_{34}O_2$. Calculated %: C 75.50; H 12.67.

The S-benzylthiouronium salt of compound (XXXII) could not be obtained.

1-Keto-8,8-dimethyl-1,2,3,4,5,6,7,8-octahydroanthracene (XXXIII). A mixture of 18.5 g of 5-keto-9,13-dimethyltetradecadien-8,12-oic acid (XXX) and polyphosphoric acid, prepared from 35 g of phosphorus pentoxide and 35 g of crystalline phosphoric acid, was heated on a boiling water bath for 3 hr; the reaction mixture was then treated with water and extracted with ether and the ether extract washed with sodium carbonate solution and water and dried with magnesium sulfate. Removal of the solvent and vacuum distillation yielded 5.3 g of a product with

b. p. 135-143° at 0.5 mm and n_D^{20} 1.5475 and a small amount of tar. Chromatography on alumina yielded 1.5 g (15%) of 1-keto-8,8-dimethyl-1,2,3,4,5,6,7,8-octahydroanthracene (XXXIII) with b. p. 132-137° at 0.4 mm and n_D^{20} 1.5492.

Found %: C 84.11, 84.33; H 8.86, 9.13. $C_{16}H_{20}O$. Calculated %: C 84.16; H 8.83.

The 2,4-dinitrophenylhydrazone had m. p. 249-250° (from a mixture of methanol and dioxane) and λ_{max} 392 mμ (in alcohol).

Found %: N 13.60, 13.57. $C_{22}H_{24}O_4N_4$. Calculated %: N 13.72.

A solution of 1.2 g of the ketone (XXXIII) in 10 ml of absolute ether was added with cooling in ice to the Grignard reagent from 0.24 g of magnesium and 1.5 g of methyl iodide in 30 ml of absolute ether. The reaction mixture was left overnight and then treated with ice and dilute hydrochloric acid and the ether layer washed with water, hyposulfite solution, and water and dried with magnesium sulfate. The alcohol (XXXVI) obtained, without further purification, was dehydrogenated over 1.1 g of 15% palladium on charcoal with heating to 320-380° for 2 hr. The cooled reaction mixture was extracted with ether and removal of the solvent yielded 0.42 g of the product (XXXVII), which was chromatographed on alumina. Elution with hexane gave 0.12 g of crystals with m. p. 123-130°, recrystallization of which from alcohol yielded 0.084 g of a product with m. p. 124-130°.

Ultraviolet spectrum: λ_{max} 222, 257, 305, 332.5, 346, 363, 383 mμ, lg ε 4.030, 5.094, 3.318, 3.36, 3.59, 3.72, 3.66 (in alcohol).

SUMMARY

1. The alkylation of dihydroresorcinol with 1-bromo-3-methyl-6-cyclohexylidenehexene-2, 1-bromo-2-cyclopentylidenethane, and 1-chloromethyl-4-isopropylbenzene gave 50-70% yields of 2-(6'-cyclohexylidene-3'-methylhexen-2'-yl)-, 2-(2'-cyclopentylidenethyl)-, and 2-(p-isopropylbenzyl)-dihydroresorcinols. The reaction of the sodium derivative of dimedone with 3-methyl-2-butenyl bromide gave 2-(3'-methyl-2'-butenyl)-dimedone.

2. Heating 2-(3',7'-dimethylocten-2'-yl)-, 2-(3',7'-dimethyloctadien-2',6'-yl)-, and 2-(3',7',11'-trimethyldodecen-2'-yl)-dihydroresorcinols with 85% phosphoric acid formed 2-methyl-2-isohexyl-, 2-methyl-2-(4'-methylpenten-3'-yl)-, and 2-methyl-2-(4',8'-dimethylnonyl)-5,7-tetrahydrochromanones.

3. Hydrolytic and reductive cleavage of 2-(2'-cyclopentylidenethyl)-, 2-(3',7'-dimethylocten-2'-yl)-, 2-(3',7'-dimethyloctadien-2',6'-yl)-, and 2-(3',7',11'-trimethyldodecen-2'-yl)-dihydroresorcinols yielded 5-keto-8-cyclopentylidenoctanoic, 8-cyclopentylidenoctanoic, 5-keto-9,13-dimethyltetradecen-8-oic, 9,13-dimethyltetradecen-8-oic, 5-keto-9,13-dimethyltetradecadien-8,12-oic, 9,12-dimethyltetradecadien-8,12-oic, 5-keto-9,13,17-trimethyloctadecen-8-oic, and 9,13,17-trimethyloctadecen-8-oic acids. By Kizhner reduction, 5-keto-8-(1'-cyclohexenyl)-octanoic acid was converted into 8-(1'-cyclohexenyl)-octanoic acid.

4. Treatment of the potassium salt of 5-keto-9,13-dimethyltetradecadien-8,12-oic acid with methylmagnesium iodide yielded farnesylacetic acid.

5. Heating 5-keto-9,13-dimethyltetradecadien-8,12-oic acid with polyphosphoric acid formed 1-keto-8,8-dimethyl-1,2,3,4,5,6,7,8-octahydroanthracene.

6. 2-(6'-Cyclohexylidene-3'-methylhexen-2'-yl)- and 2-(p-isopropylbenzyl)-dihydroresorcinols, 2-(3'-methyl-2'-butenyl)-dimedone, the methyl ether of 2-(3',7'-dimethylocten-2'-yl)-dihydroresorcinol, the enol acetates of 2-(6'-cyclohexylidene-3'-methylhexene-2'-yl)- and 2-(p-isopropylbenzyl)-dihydroresorcinols, the enol acetate of 2-(3'-methyl-2'-butenyl)-dimedone, 2-methyl-3-isohexyl-5,7-tetrahydrochromanone-5, and 5-keto-8-(1'-cyclohexenyl)-octanoic acid were tested for bacteriostatic, fungistatic, antiviral, and anthelminthic action.

2-Methyl-2-isohexyl-5,7-tetrahydrochromanone-5, 2-methyl-2-(4',8'-dimethylnonyl)-5,7-tetrahydrochromanone-5, and the methyl ether of 2-(3',7'-dimethylocten-2'-yl)-dihydroresorcinol have appreciable activity towardtuberculosis bacilli (human type, strain Academia), but this is sharply reduced in a medium containing serum. An anthelminthic action in vitro was shown by only 2-(6'-cyclohexylidene-3'-methylhexen-2'-yl)-dihydroresorcinol and the enol acetates of 2-(6'-cyclohexylidene-3'-methylhexen-2'-yl)- and 2-(p-isopropylbenzyl)-dihydroresorcinols. Antiviral activity in vitro was shown by 5-keto-9,13,17-trimethyloctadecen-8-oic, 8-13-dimethyltetradecen-8-oic, and 9,13,17-trimethyloctadecen-8-oic acids.

LITERATURE CITED

1. V. I. Gunar, S. I. Zav'yalov, A. I. Krotov, Izv. AN SSSR, OKhN 1960, 536.
2. S. I. Zav'yalov, V. I. Gunar, G. N. Pershin, S. N. Milovanova, Izv. AN SSSR, OKhN 1960, 1241.
3. L. S. Leder-Pakendorf, DAN SSSR 31, 756 (1941); L. S. Bondar', R. A. Okunev, Trans. VIII Mendeleev Conference, Org. Chemistry and Technol. Section [in Russian] 185 (1959).
4. T. Moroe et al., J. Pharm. Soc. Japan 71, 543 (1951); Chem. Abs. 45, 9116 (1951).
5. D. Vorländer, A. Knötzsh, Lieb. Ann. 284, 317 (1897); D. Vorländer, F. Kalkow, Lieb. Ann. 309, 356 (1899).
6. H. Stätter, W. Dierichs, Ber. 85, 290 (1952).
7. S. I. Zav'yalov, V. I. Gunar, L. F. Kudryavtseva, Izv. AN SSSR, OKhN 1960, 2010.
8. V. I. Gunar, S. I. Zav'yalov, Izv. AN SSSR, OKhN 1960, 937.
9. V. I. Gunar, S. I. Zav'yalov, DAN SSSR 132, 829 (1960).
10. Y. Naves, P. Ardizio, Bull. Soc. Chim. 1954, 661: F. Zobrist, H. Schinz, Helv. Chim. Acta. 32, 1192 (1949); Y. Naves, Helv. Chim. Acta. 32, 1802 (1949); A. Calieses, H. Schinz, Helv. Chim. Acta. 35, 1649 (1952).
11. I. Koo, J. Am. Chem. Soc. 72, 1891 (1953).
12. B. A. Kazanskii, A. L. Liberman, Izv. AN SSSR, OKhN 1947, 265; R. Linstead, S. Thomas, J. Chem. Soc. 1940, 1127; H. Adkins, J. Davis, J. Am. Chem. Soc., 71, 2956 (1948).
13. A. S. Cherkasov, ZhOKh 29, 2209 (1959); W. Nes, E. Mosettig, J. Am. Chem. Soc. 76, 3182 (1954); G. Clemo, N. Chatge, J. Chem. Soc. 1956, 1068; W. Mosby, J. Org. Chem. 18, 964 (1953).
14. F. Askew, J. Chem. Soc. 1935, 509; A. Gillem and E. Stern, Electronic Absorption Spectra of Organic Compounds [Russian translation] IL (1957).
15. I. N. Nazarov, S. M. Makin, V. B. Mochalin, D. V. Nazarova, V. P. Vinogradov, B. K. Kruptsov, I. I. Nazarova, O. A. Shavrygina, DAN SSSR 114, 1242 (1957).
16. G. Stork, A. Burgstahler, J. Am Chem. Soc. 77, 5068 (1955).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ANTHRAQUINONE DERIVATIVES

I. SYNTHESIS OF CHLORO DERIVATIVES OF 2-ANTHRAQUINONECARBOXYLIC ACID

N. S. Dokunikhin, Z. Z. Moiseeva, and S. N. Burenko

Scientific Research Institute of Organic Intermediates and Dyes

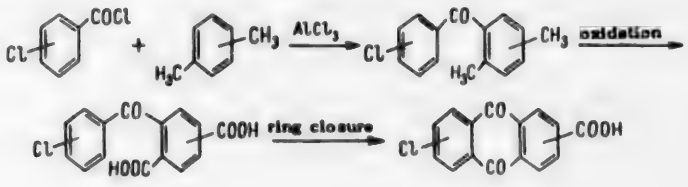
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3985-3987, December, 1961
Original article submitted August 23, 1960

Anthraquinone derivatives containing a halogen and a carboxyl group in different benzene rings of the anthraquinone nucleus are of interest as intermediates for dyes.

The methods of preparing such compounds described in the literature are either complicated or lead to isomers or compounds with the substitutents in unknown positions [1]. Only 5,8-dichloroanthraquinone-2-carboxylic acid may be prepared reliably by the methods described [2].

In contrast to all those mentioned, the method proposed here makes it possible to obtain mono- and dichloro derivatives of anthraquinone-2-carboxylic acid with the chlorine atom in any position of the other benzene ring of anthraquinone.

The synthesis was achieved according to the scheme:



EXPERIMENTAL

Preparation of ketone. To a suspension of 0.8 mole of $AlCl_3$ in 500 ml of p- or m-xylene was added 0.39 mole of chlorobenzoyl chloride and the mixture heated at 60° for 1 hr. The cooled mixture was poured into 500 ml of iced water and 50 ml of concentrated hydrochloric acid, the xylene layer separated and washed with water, the xylene removed, and the ketone vacuum distilled (Table 1).

Preparation of benzophenonedicarboxylic acids. a) Oxidation of ketones with bichromate in sulfuric acid and then permanganate in an alkaline medium. To a solution of 0.1 mole of the ketone in 190 ml of 80% H_2SO_4 was added a solution of 114 g of potassium bichromate in 51 ml of water and the mixture heated at 80° for 1 hr. The reaction mixture was poured into 1200 ml of iced water and the precipitate collected, washed with water, pressed out, and added to a solution of 18 g of NaOH in 900 ml of water. The mixture was heated to 70°, 22.7 g of $KMnO_4$ added, the mixture then heated at 100° for 1 hr and filtered, the filtrate acidified with hydrochloric acid, and the precipitate collected, washed with water, and dried. The yield was 70-80% (Table 2).

b) Oxidation with nitric acid. A mixture of 0.001 mole of the ketone, 6.3 ml of HNO_3 (d 1.29) and 9.5 ml of water was heated in a sealed tube at 195-200° for 5 hr. After the mixture had been cooled, the precipitate was collected, washed with water, and dried. The yield was 85-90% (Table 2).

Preparation of chloro derivatives of 2-anthraquinonecarboxylic acid. A solution of 0.025 mole of the chloro-substituted benzophenonedicarboxylic acid in a mixture of 13 ml of 10% oleum and 19 ml of sulfuric acid mono-

TABLE 1

Compound	Boiling point (pressure in mm)	Empirical formual	d^{20}_{20}	$n^{20}D$	Found		Calculated	
					% Cl	MR_D	%Cl	MR_D
2-Chloro-2',4'-dimethylbenzophenone	200-204°(8)•	$C_{15}H_{13}OCl$	1.16	1.597		71.45		69.15
2-Chloro-2',5'-dimethylbenzophenone	186-190(2)	$C_{15}H_{13}OCl$	1.16	1.595		71.34		60.15
4-Chloro-2',4'-dimethylbenzophenone	M.p. 41.5-42°(from alcohol)••	$C_{15}H_{13}OCl$			14.45,14.62		14.52	
4-Chloro-2',5'-dimethylbenzophenone	171-172 (2), m.p. 40-40.5° (from alcohol)	$C_{15}H_{13}OCl$			14.58••• 14.54		14.52	
2,4-Dichloro-2',5'-dimethylbenzophenone	184-186 (4)	$C_{15}H_{12}OCl_2$	1.290	1.607		74.39		73.83

•According to literature data: b.p. 218°(40 mm) [3].

•• According to literature data: m.p. 44°[3].

•••Found %: C 73.64, 73.75; H 5.25, 5.20. Calculated %: C 73.62; H 5.32.

TABLE 2

Compound	Melting point (from glacial acetic acid)	Empirical formula	Found (%)			Calculated (%)		
			C	H	Cl	C	H	Cl
2-Chlorobenzophenone-2',4'-dicarboxylic acid	306-309°	$C_{15}H_9O_5Cl$	59.67,59.40	2.96,3.03	11.86,11.59	59.22	2.99	11.63
2-Chlorobenzophenone-2',5'-dicarboxylic acid	280-282.5	$C_{15}H_9O_5Cl$	59.03,59.28	3.30,3.35	11.56,11.23	59.22	2.99	11.63
4-Chlorobenzophenone-2',4'-dicarboxylic acid	272-273	$C_{15}H_9O_5Cl$	60.18,60.06	3.24,3.22	11.25,11.23	59.22	2.99	11.63
4-Chlorobenzophenone-2',5'-dicarboxylic acid	288-291	$C_{15}H_9O_5Cl$	58.90,58.70	2.95,3.09	10.88,10.93	59.22	2.99	11.63
2,4-Dichlorobenzophenone-2',5'-dicarboxylic acid	288.5-290	$C_{15}H_8O_5Cl_2$	53.25,53.06	2.53,2.69	20.84,20.72	53.09	2.36	20.94

hydrate was heated at 130-140° for 2 hr, cooled, and poured onto ice and water and the precipitate collected, washed, and dried. The yield was 72-82% (Table 3).

TABLE 3

Compound	Melting point (recrystallization solvent)	Empirical formula	% Cl	
			found	calcu.
5-Chloroanthraquinone-2-carboxylic acid	308-310° (glacial acetic acid or HNO_3, d 1.4)	$C_{15}H_7O_4Cl$	11.56,11.56	12.36
6-Chloroanthraquinone-2-carboxylic acid	333.5-335 (glacial acetic acid)	$C_{15}H_7O_4Cl$	12.63,11.99	12.36
7-Chloroanthraquinone-2-carboxylic acid	336-339 (HNO_3 d 1.4)	$C_{15}H_7O_4Cl$	12.02,12.07	12.36
8-Chloroanthraquinone-2-carboxylic acid	323-324 (glacial acetic acid)	$C_{15}H_7O_4Cl$	12.23,11.93	12.36
5,7-Dichloroanthraquinone-2-carboxylic acid	294-295.5 (nitrobenzene)	$C_{15}H_6O_4Cl_2$	22.30,22.32	22.12

SUMMARY

A method was developed for the synthesis of chloro derivatives of anthraquinone-2-carboxylic acid containing the chlorine atom and carboxyl group in different benzene rings of the anthraquinone nucleus.

LITERATURE CITED

1. Germ. Pat. 570859; Friedl. 19, 1922; W. Lawrance, J. Am. Chem. Soc. 43, 2578 (1921); A. Eckert, Monatsh. 35, 292 (1914); W. Perkin, J. Chem. Soc. 65, 844 (1894).
2. Germ. Pat. 255121; Friedl. 11, 596; A. Eckert, J. pr. Ch. 702, 335 (1921).
3. Germ. Pat. 481819; Friedl. 16, 717; Germ. Pat. 267271; Friedl. 11, 2015.

XV. CHEMICAL PROPERTIES OF 1,3-DICHLOROCYCLOHEXADIENE-1,3 AND ITS DERIVATIVES

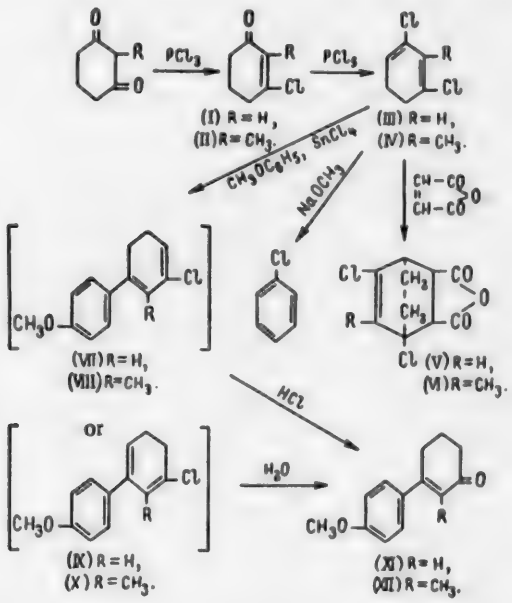
S. I. Zav'yalov and G. V. Kondrat'eva

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

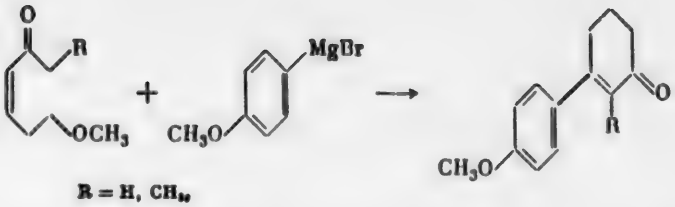
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3987-3991, December, 1961
Original article submitted December 14, 1960

It was established previously [1] that the action of phosphorus pentachloride on dihydroresorcinol forms smoothly 1,3-dichlorocyclohexadiene-1,3 (III), which contains the system of the unknown 1,3-dichlorobutadiene. In a study of the chemical properties of this dichloride, it was found that it is aromatized readily by sodium in amyl alcohol [2] or bromine [1] to give benzene in the first case and 1,3-dichlorobenzene in the second. It was also shown [2] that sodium in moist ether produces dehalogenation and reduction of 1,3-dichlorocyclohexadiene-1,3 to form a mixture of cyclohexadiene-1,3 and cyclohexene.

As a continuation of these investigations, in the present work we studied some new conversions of 1,3-dichlorocyclohexadiene-1,3 and its derivatives which involve the halogen atoms and double bonds.



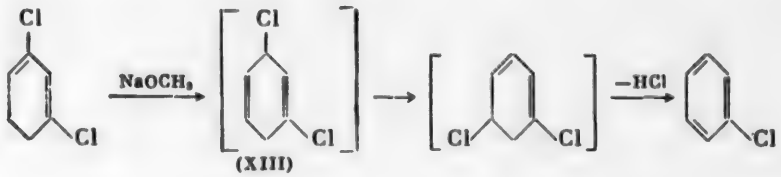
1,3-Dichlorocyclohexadiene-1,3 and its 2-methyl derivative (IV), which was prepared by the action of phosphorus pentachloride on 2-methylhydroresorcinol, undergo diene synthesis with maleic anhydride when the reagents are heated briefly to 180-200°. The reaction of the dichlorides (III) and (IV) with anisole in the presence of stannic chloride with subsequent acid hydrolysis of the intermediate bicyclic chlorides (VII or IX) and (VIII or X), which were not isolated in a pure form, formed the unsaturated bicyclic ketones (XI) and (XII). The latter were synthesized previously [3,4] from enol ethers of dihydroresorcinol and 2-methyldihydroresorcinol according to the following scheme:



R = H, CH_3

3-Chlorocyclohexen-2-one-1 (I) [1] and 2-methyl-3-chlorocyclohexen-2-one-1 (II), which were obtained by the action of phosphorus trichloride on dihydroresorcinol and 2-methyldihydroresorcinol, did not undergo a Friedel–Crafts reaction with anisole under the above conditions.

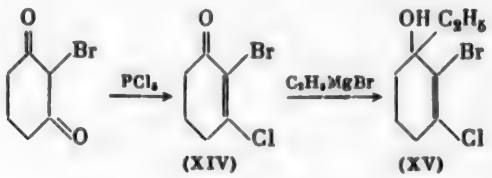
The dichlorides (III) and (IV) did not undergo substitutions when treated with such nucleophilic reagents as alkali and alcoholates. When boiled for 4 hr with a methanol solution of sodium methylate, the dichloride (III) underwent dehydrochlorination and aromatization to form chlorobenzene. This reaction probably includes a prototropic displacement of the double bond with the formation of the intermediate 1,3-dichlorocyclohexadiene-1,4 (XIII) and subsequent allyl migration of the halogen atom.



(XIII)

2-Methyldichlorocyclohexadiene-1,3 did not react with sodium methylate when boiled in methanol for 4 hr. Both the dichlorides (III) and (IV) were almost unchanged when treated with alkali in boiling methanol (4 hr) or when heated with diethylaniline to 180-200°.

The preparation of chloro ketones of types (I) and (II) from dihydroresorcinol and its derivatives is known [1] to require phosphorus trichloride and not phosphorus pentachloride as the latter readily attacks both keto groups of a cyclic β-diketone. We found that an exception to this rule is 2-bromodihydroresorcinol, which smoothly gives 2-bromo-3-chlorocyclohexen-2-one-1 (XIV) even with excess phosphorus pentachloirde at room temperature. Carrying out this reaction in boiling benzene yielded a liquid mixture of halogen derivatives which was not studied in more detail. The carbonyl group of 2-bromo-3-chlorocyclohexen-2-one-1 has a marked ketonic nature as this compound smoothly undergoes a Grignard reaction and gives a 2,4-dinitrophenylhydrazone.



(XIV) (XV)

EXPERIMENTAL

1,3-Dichlorocyclohexadiene-1,3 (III) (b. p. 56-60° at 6 mm and n_D^{17} 1.5340) was obtained by the action of phosphorus pentachloride on dihydroresorcinol in chloroform [1].

3-Chlorocyclohexen-2-one-1 (I) (b. p. 78-80° at 7 mm and n_D^{20} 1.5180) was prepared by treatment of dihydroresorcinol with phosphorus trichloride in chloroform [1].

2-Methyl-1,3-dichlorocyclohexadiene-1,3 (IV). To 20 g of phosphorus pentachloride in 100 ml of anhydrous benzene was added 6.3 g of 2-methyldihydroresorcinol in portions with stirring. The solution obtained was left at room temperature for 1 hr and then washed with water. After removal of the benzene, the residue was vacuum distilled. We obtained 5.2 g (64%) of 2-methyl-3-dichlorocyclohexadiene-1,3 (IV) with b. p. 96-97° at 27 mm and n_D^{20} 1.5310.

The substance was very unstable and could be stored for a few days only at low temperatures (−60−70°).

Found %: C 52.08, 52.28; H 4.75, 4.66; Cl 43.18, 42,98. $C_7H_8Cl_2$. Calculated %: C 51.57; H 4.93; Cl 43.49.

2-Methyl-3-chlorocyclohexen-2-one-1 (II). A mixture of 10 g of 2-methyldihydroresorcinol and 3.8 g of phosphorus trichloride in 30 ml of chloroform was boiled for 3 hr. The cooled solution was washed with water, dried with magnesium sulfate, and evaporated. Vacuum distillation of the residue yielded 6.7 g (56%) of 2-methyl-3-chlorocyclohexen-2-one-1 (II) with b. p. 83-84° at 7 mm and n_D^{20} 1.5172.

Found %: C 57.64, 57.79; H 6.39, 6.51; Cl 24.07, 24.11. C_7H_9OCl. Calculated %: C 58.14; H 6.23; Cl 24.57.

Reaction of 1,3-dichlorocyclohexadiene-1,3 with maleic anhydride. A mixture of 15 g of 1,3-dichlorocyclohexadiene-1,3 and 10 g of maleic anhydride was heated at 145-150° for 10-15 min. When the exothermal reaction had ceased, the temperature was raised to 190°. The oil obtained was cooled and dissolved in ether. On standing, the solution deposited 11 g (65%) of the adduct (V) with m. p. 109-110° (from a mixture of benzene and heptane).

Found %: C 48.80, 48.50; H 3.13, 3.03; Cl 28.40, 28.30. $C_{10}H_8O_3Cl_2$. Calculated %: C 48.77; H 2.85; Cl 28.84.

Reaction of 2-methyl-1,3-dichlorocyclohexadiene-1,3 with maleic anhydride. From 1.7 g of 2-methyl-1,3-dichlorocyclohexadiene-1,3 and 1 g of maleic anhydride, as described above, we obtained 1.3 g (48%) of the adduct (VI) with m. p. 135-137° (from a mixture of benzene and heptane).

Found %: C 50.62, 50.75; H 3.89, 3.99; Cl 27.45, 27.43. $C_{12}H_{10}O_3Cl_2$. Calculated %: C 50.59; H 3.86; Cl 27.15.

Reaction of 1,3-dichlorocyclohexadiene-1,3 with anisole in the presence of stannic chloride. To a solution of 8.5 g of stannic chloride in 30 ml of benzene were added successively 3 g of anisole and 5 g of 1,3-dichlorocyclohexadiene-1,3 in 10 ml of benzene with stirring. The mixture was treated with 5% hydrochloric acid and then left at room temperature for 12 hr. The benzene solution was evaporated and the residue vacuum distilled. We obtained 2.5 g of product with b. p. 180-200° at 2 mm, which was dissolved in ether and the solution cooled with a mixture of solid carbon dioxide and acetone. This yielded 1.2 g (18%) of the ketone (XI) with m. p. 83-84° (from a mixture of benzene and heptane). The ketone (XI) and its 2,4-dinitrophenylhydrazone (m. p. 191-193°) did not depress the melting points of corresponding samples prepared by a known method [3].

Reaction of 2-methyl-1,3-dichlorocyclohexadiene-1,3 with anisole in the presence of stannic chloride. By the above procedure, from 4 g of 2-methyl-1,3-dichlorocyclohexadiene-1,3, 2.7 g of anisole, and 6.7 g of stannic chloride we obtained 0.5 g (10%) of the ketone (XII) with m. p. 60-62° (from heptane) which did not depress the melting point of an authentic sample [4].

Reaction of 1,3-dichlorocyclohexadiene-1,3 with sodium methylate. A mixture of 6 g of 1,3-dichlorocyclohexadiene-1,3 and a solution of sodium methylate prepared from 2.3 g of sodium and 30 ml of methanol was boiled for 4 hr. The cooled solution was diluted with ether, washed with water, and evaporated. Distillation of the residue gave 2 g (44%) of chlorobenzene with b. p. 131-132° and m. p. −45−43°.

2-Bromo-3-chlorocyclohexen-2-one-1. To 60 g of phosphorus pentachloride in 200 ml of ether was added 40 g of 2-bromodihydroresorcinol and the mixture left at room temperature for 5 hr. After evaporation of the solvent, the residue was treated with water and the precipitate collected. We obtained 30 g (68%) of 2-bromo-3-chlorocyclohexen-2-one-1 (XIV) with m. p. 68-69° (from hexane).

Found %: C 36.64, 36.70; H 2.43, 2.56; Cl + Br 54.83, 54.92. C_6H_6OClBr. Calculated %: C 36.75; H 2.89; Cl + Br 55.13.

The 2,4-dinitrophenylhydrazone had m. p. 180-181° (decomp.).

Found %: N 16.81, 16.94. $C_{12}H_{10}N_4ClBr$. Calculated %: N 17.20.

Reaction of 2-bromo-3-chlorocyclohexen-2-one-1 with ethylmagnesium bromide. To a solution of ethylmagnesium bromide (from 1 g of magnesium) in 40 ml of ether was added 6 g of 2-bromo-3-chlorocyclohexen-2-one-1 in portions and the mixture left at room temperature for 0.5 hr. Treatment with ice and dilute hydrochloric acid yielded 5.5 g (80%) of the alcohol (XV) with b.p. 126-128° at 4 mm and n_D^{20} 1.5461.

Found %: Cl + Br 48.02, 48.31. $C_8H_{12}OClBr$. Calculated %: Cl + Br 48.20.

SUMMARY

1. 1,3-Dichlorocyclohexadiene-1,3 and 2-methyl-1,3-dichlorocyclohexadiene-1,3 undergo diene synthesis with maleic anhydride.

2. The action of anisole on 1,3-dichlorocyclohexadiene-1,3 and 2-methyl-1,3-dichlorocyclohexadiene-1,3 in the presence of stannic chloride and subsequent acid hydrolysis forms 3-(p-methoxyphenyl)-cyclohexen-2-one-1 and 2-methyl-3-(p-methoxyphenyl)-cyclohexen-2-one-1, respectively.

3. When heated with sodium methylate in boiling methanol, 1,3-dichlorocyclohexadiene-1,3 is converted into chlorobenzene.

4. 2-Bromodihydroresorcinol is converted into 2-bromo-3-chlorocyclohexen-2-one-1 by treatment with phosphorus pentachloride.

LITERATURE CITED

1. A. Crossley, P. Haas, J. Chem. Soc. 83, 498, 501 (1903).
2. A. Crossley, J. Chem. Soc. 85, 1411 (1904).
3. I. N. Nazarov, G. V. Aleksandrova, S. I. Zav'yalov, Izv. AN SSSR, OKhN 1959, 1967.
4. G. V. Kondrat'eva, L. F. Kudryavtseva, S. I. Zav'yalov, ZhOKh 31, 3695 (1961).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ARYLTRIFLUOROMONOHYDRIDES OF PHOSPHORUS

Zh. M. Ivanova and A. V. Kirsanov

Institute of Organic Chemistry, Academy of Sciences, Ukrainian SSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3991-3994, December, 1961
Original article submitted January 6, 1961

Very few difluorophosphines are known [1, 2] and their properties have not been studied. In an attempt at the preparation of phenyldifluorophosphine from phenyldichlorophosphine and antimony trifluroide, phenyltetrafluorophosphorus and metallic antimony were obtained in high yield [3]. This reaction demonstrates that phenyldifluorophosphine is a stronger reducing agent than phenyldichlorophosphine, which is not oxidized by antimony trichloride, or that antimony trifluoride is a stronger oxidizing agent in this case than antimony trichloride (see below). V. N. Kulakova, Yu. M. Zinov'ev, and L. Z. Soborovskii [2] reported that they were able to obtain phenyldifluorophosphine in 14% yield from phenyldichlorophosphine and antimony trifluoride in ether, but they did not give the properties of phenyldifluorophosphine, apart from the boiling point, or any data demonstrating the structure of the phenyldifluorophosphine they obtained. The wide boiling range (64-70°) raised doubts as to the individuality of this preparation. We therefore repeated the experiments of these authors [3] exactly according to their description. We obtained only a few drops of a fraction with b. p. 64-70° and the bulk of the reaction product was found to be phenyltetrafluorophosphorus. Thus, we were unable to reproduce their experiments and could not obtain phenyldifluorophosphine by the procedure they described.

In order to prepare aryldifluorophosphines, we studied the reaction of aryldichlorophosphines with various inorganic fluorides. There was a vigorous reaction when aryldichlorophosphines were heated with potassium bifluoride at 50-60°. If the process was carried out at 20-40 mm, there distilled colorless, clear liquids with a strong odor of phosphine, which fumed in air, attacked glass, and distilled without decomposition at 40 mm. According to the fluorine and phosphorus content, their composition corresponded to the formula $ArPF_3H$. Thus, in the reaction of aryldichlorophosphines with potassium bifluoride there is not only the exchange of two chlorine atoms for fluorine, but also the addition of a hydrogen fluoride molecule to form aryltrifluoromonohydrides of phosphorus (Table 1) which could also be regarded as molecular compounds of aryldifluorophosphines and hydrogen fluoride $ArPF_2 \cdot HF$ or as salt-like compounds $(ArPF_2H)^+F^-$. However, the comparatively low boiling points and stability during distillation indicate that these substances cannot be of a salt-like nature and are not molecular compounds.

$$ArPCl_2 + 2KHF_2 \rightarrow 2KCl + HF + ArPF_3H$$

TABLE 1. Aryltrifluoromonohydrides of Phosphorus $ArPF_3H$

Ar	Yield %	Boiling pt. (pressure in mm)	Found %		Empirical formula	Calculated %	
			P	F		P	F
C_6H_5	84	57—58°(20)	18.51, 18.63	33.70, 34.70	$C_6H_6PF_3$	18.70	34.38
$p\text{-}CH_3C_6H_4$	79	90—91(40)	17.36, 17.60	31.62, 31.29	$C_7H_8PF_3$	17.24	31.70
$p\text{-}ClC_6H_4$	90	90—91(35)	15.44, 15.15	28.33, 28.00	$C_6H_5PF_3Cl$	15.41	28.42

The structure of the aryltrifluoromonohydrides of phosphorus was also confirmed by chemical conversions. When treated with water, they were converted almost quantitatively into the corresponding arylphosphinous acids

$$ArPF_3H + 2H_2O \rightarrow 3HF + ArP(OH)_2.$$

and, when treated with sulfur, they gave yields of more than 90% of the diacid fluorides of the corresponding arylthiophosphinic acids.

$$ArPF_2H + S \rightarrow HF + ArPSF_2$$

When heated with antimony trichloride, the aryltrifluoromonohydrides of phosphorus were unchanged, but were readily oxidized by antimony trifluoride (cf. above), which was reduced to metallic antimony.

$$SbF3 \xrightarrow{+ArPF_2H} Sb$$

When treated with chlorine, aryltrifluoromonohydrides of phosphorus were oxidized with the evolution of heat and the formation of a mixture of mixed aryltetrachlorofluorophosphoruses, which were converted into the corresponding arylphosphinic acids in 85% yield by hydrolysis.

$$ArPF_2H + Cl_2 \rightarrow HF + [ArPF_{0-4}\,Cl_{4-0}] \xrightarrow{+H_2O} ArPO(OH)_2.$$

The action of equivalent amounts of alcohol and triethylamine on the diacid fluroide of p-chlorophenylthiophosphinic acid (cf. [4]) yielded acid fluorides of monoesters of p-chlorophenylthiophosphinic acid (Table 2), which were clear colorless liquids. They dissolved readily in the normal organic solvents, were insoluble in water, did not attack glass in the absence of moisture, were hydrolyzed very slowly by water at 20°, had the properties of active contact insecticides, and had a comparatively low toxicity toward warm-blooded animals.

$$p\text{-}ClC_6H_4PSF_2 \xrightarrow[+\,N(C_2H_5)_3]{+\,ROH} p\text{-}ClC_6H_4PS(OR)F$$

TABLE 2. Acid Fluorides of Monoesters of p-Chlorophenylthiophosphinic Acid p-$ClC_6H_4PS(OR)F$

R	Yield %	Boiling pt. (pressure in mm)	d^{18}_{20}	n^{18}_D	Found %		Empirical formula	Calculated %	
					MR_D	% P		MR_D	% P
CH_3	48	109—110°(4)	1.3574	1.5584	53.35	13.80, 13.75	$C_7H_7OPSFCl$	53.23	13.80
C_2H_5	80	133—134(10)	1.2957	1.5350	57.33	13.21, 13.30	$C_8H_9OPSFCl$	57.85	13.00
iso-C_3H_7	65	125—126(4)	1.2452	1.5330	62.93	12.42, 12.15	$C_9H_{11}OPSFCl$	62.47	12.31

EXPERIMENTAL

Aryltrifluoromonohydrides of phosphorus (Table 1). A mixture of 0.2 mole of the aryldichlorophosphine and 0.4 mole of potassium bifluoride contained in a platinum or quartz round-bottomed flask connected to a condenser and receiver was heated in vacuum until a vigorous reaction began (50-60°) and the heat source then removed. The aryltrifluoromonohydrides of phosphorus formed distilled as a result of the heat of reaction. The aryltrifluoromonohydrides of phosphorus were purified by distillation in nitrogen under reduced pressure in a platinum or quartz apparatus.

Hydrolysis of p-chlorophenyltrifluoromonohydride of phosphorus. To 0.1 mole of the substance in a platinum dish was added 40 ml of water. The temperature of the mixture rose as a result of the heat of reaction and a crystalline precipitate of p-chlorophenylphosphinous acid formed after a few minutes. The water was evaporated completely at room temperature in a vacuum desiccator over potassium hydroxide and sulfuric acid and then over potassium hydroxide and phosphorus pentoxide. The yield of p-chlorophenylphosphinous acid was quantitative and after recrystallization from water, the substance had m. p. 129-130°, which corresponds to literature data [5].

Addition of sulfur to p-chlorophenyltrifluoromonohydride of phosphorus. A mixture of 0.03 mole of the p-chlorophenyltrifluoromonohydride of phosphorus and 0.03 g-at of sulfur was heated in a quartz flask with a reflux condenser to 140-150° on an oil bath for 15 min and the reaction mixture vacuum distilled. The yield of the diacid fluoride of p-chlorophenylthiophosphinic acid was 96% and the product had b. p. 114-115°(40 mm) and n_D^{20} 1.5390, which correspond to literature data [3].

Reaction of phenyltrifluoromonohydride of phosphorus with chlorine. A 0.06-mole sample of the phenyltrifluoromonohydride of phosphorus was placed in a quartz Claisen flask and saturated with chlorine while cooled with water and ice. The reaction was accompanied by the evolution of heat. The reaction product, which consisted of a mixture of mixed aryltetrachlorofluorophosphoruses, was vacuum distilled and had b. p. 67-140° (50 mm). For identification, the distillate was hydrolyzed with water (the reaction proceeded very vigorously) and the phenylphosphinic acid isolated by the usual method. The yield was 87% and the m. p. 162-163° and the product was identified by a mixed melting point.

Acid fluorides of monoesters of p-chlorophenylthiophosphinic acid (Table 2). To a solution of 0.1 mole of the diacid fluoride of p-chlorophenylthiophosphinic acid in 20 ml of absolute ether was added a mixture of 0.1 mole of alcohol, 0.1 mole of triethylamine, and 10 ml of ether with vigorous stirring and cooling with water and ice. After 12 hr, the reaction mixture was washed with water to remove triethylamine hydrofluoride, the ether solution dried with sodium sulfate, the ether removed, and the residue vacuum distilled.

SUMMARY

The action of potassium bifluoride on aryldichlorophosphines forms aryltrifluoromonohydrides of phosphorus. Their structure was demonstrated by chemical conversions: they give arylphosphinous acids on hydrolysis and diacid fluorides of arylthiophosphinic acids when treated with sulfur.

LITERATURE CITED

1. F. Seel, H. Jonas, L. Richl, J. Langer, Ang. Chem. 67, 32 (1955); J. van Wazer, C. Callis, J. Shoolery, R. Jones, J. Am. Chem. Soc. 78, 5715 (1956); A. Burg, G. Brendel, J. Am. Chem. Soc. 80, 3198 (1958); R. N. Sterlin, R. D. Yatsenko, L. D. Pinkina, I. L. Knunyants, Izv. AN SSSR, OKhN 1960, 1991.
2. V. N. Kulakova, Yu. M. Zinov'ev, L. Z. Soborovskii, ZhOKh 29, 3957 (1959).
3. L. M. Yagupol'skii, Zh. M. Ivanova, ZhOKh 29, 3767 (1959).
4. L. M. Yagupol'skii, Zh. M. Ivanova, ZhOKh 30, 1284 (1960).
5. G. Kosolapoff, Organophosphorus Compounds. 147 (1950).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

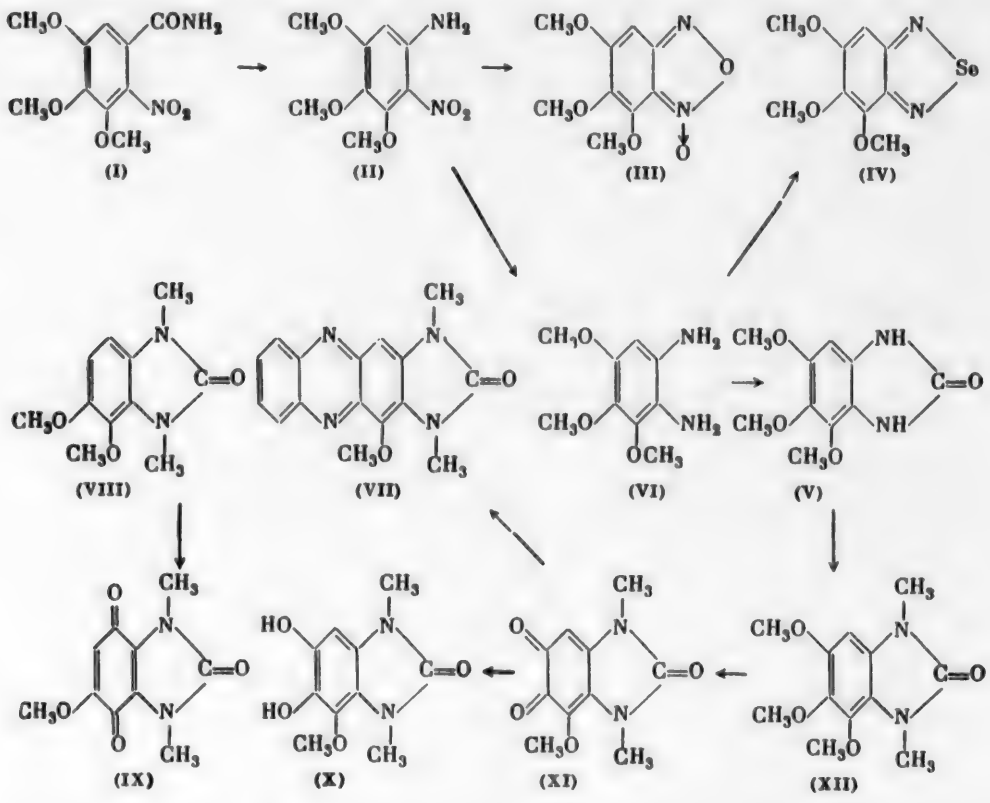
IMIDAZOLE DERIVATIVES. XXVI.

A. V. El'tsov and L. S. Éfros

Lensovet Leningrad Technological Institute

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 3994-4001, December, 1961
Original article submitted January 24, 1961

In studying the oxidative conversions of methoxy derivatives of benzimidazolone, we observed the formation of a methoxyquinone $C_{10}H_{10}O_4N_2$ with m. p. 206.5° by the action of cerium sulfate on 1,3-dimethyl-4,5-dimethoxybenzimidazolone (VIII) [1-3]. On the basis of certain properties of this methoxyquinone, of the two possible structures of the ortho- and para-quinones (XI and IX), we choose the latter for this compound. This direction of the cleavage of the product (VIII) seemed particularly interesting to us and therefore we attempted to synthesize the quinone (XI) in order to eliminate completely the possibility of this structure for the quinone with m. p. 206.5°.



We proposed to prepare the quinone (XI) by oxidation of the trimethoxy derivative (XII). We then had no fear of the formation of the isomeric compound 1,3-dimethyl-4,5-dioxo-6-methoxybenzimidazolone, as the 4,5-dimethoxy derivative (VIII) was not oxidized to the 4,5-quinone under mild conditions and was converted into a quinone containing one methoxyl group under drastic conditions [3].

For the synthesis of compound (XII), the amide of nitrotrimethylgallic acid (I) was treated with sodium hypochlorite to give an 87% yield of the nitroaniline (II);* a slight excess of hypochlorite led to the formation of the trimethoxybenzofuroxane (III), which was also formed smoothly by boiling the nitroaniline (II) with sodium hypochlorite. The infrared spectrum of the benzofuroxane (III) (Fig. 1) contained bands characteristic of the vibrations of a $C{=}N\langle^{\nearrow}_{\searrow}$ — group (1626 cm^{-1}), a C = N group (1583 cm^{-1}), and a N − O group (1321 cm^{-1}) [5]. The frequency 861 cm^{-1} may be assigned to vibrations of the C–H bonds of the benzene nucleus containing 5 substitutents.

Catalytic hydrogenation of the nitroaniline (II) over PtO_2 gave the diamine (VI), which was characterized as the selenodiazole derivative (IV), and fusion of the diamine with urea gave 3,5,6-trimethoxybezimidazolone (V). When treated with dimethyl sulfate, the latter formed the 1,3-dimethyl derivative (XII).

By treatment with ferric chloride and nitrous acid, compound (XII) was converted into the quinone (XI) with m. p. 198°, which strongly depressed the melting point of the quinone with m. p. 206.5°. Treatment of the quinone (XI) with a reducing agent readily gave the leuco compound (X) and the reaction with o-phenylenediamine gave the azine (VII), which contains a methoxyl group like the starting quinone.

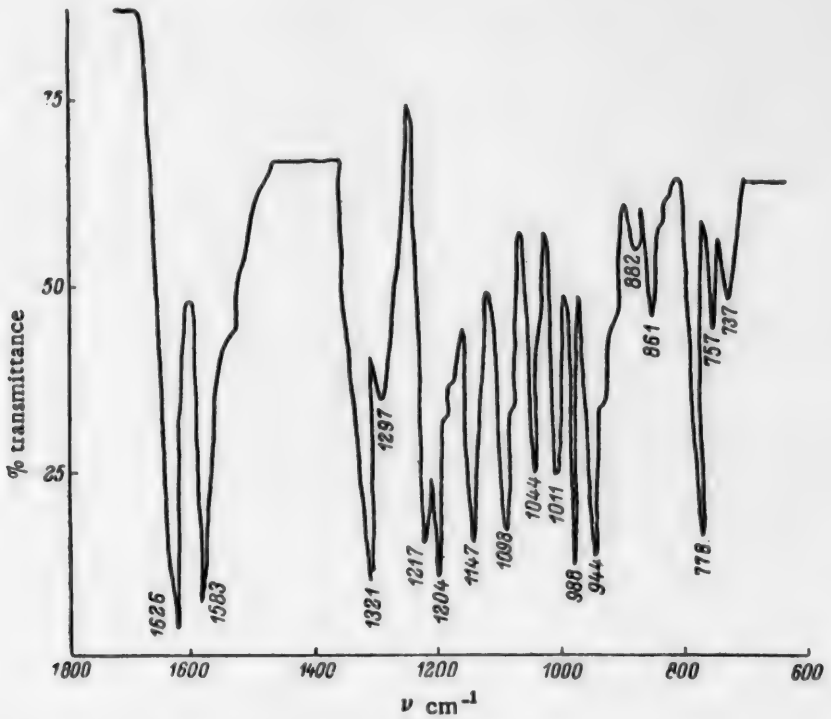
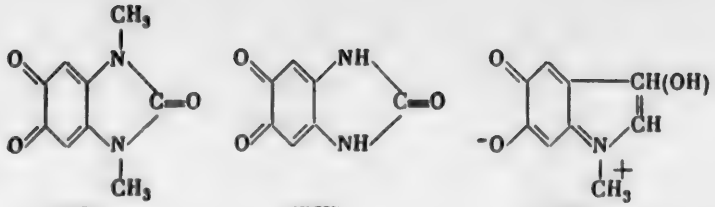


Fig. 1. Infrared spectrum of 4,5,6-trimethoxybenzofuroxane (III) in vaseline oil.

The quinone (XI), like 1,3-dimethyl-5,6-dioxobenzimidazolone (XIII) [1], has clearly expressed solvatochromic properties. In this case, in comparison with the quinone (XIII), an over-all bathochromic displacement of the light absorption is observed. For the long-wave absorption, this displacement in aqueous solution equals 50 mμ and in carbon tetrachloride solution, 55 mμ (Fig. 2, cf. [1]).

*Elderfield and Kruger obtained the nitroaniline (II) in 26% yield by using sodium hypobromite [4].



(XIII) (XIV) (XV)

In explaining the solvatochromism of 1,3-dimethyl-5,6-dioxobenzimidazolone (XIII) and its derivatives by a change in the polarization of the molecule through the system of conjugated bonds under the influence of the solvent we compared it with adrenochrome, which exists in the intraionoid form (XV) [6]. The infrared spectrum of adrenochrome was found to contain intense bands at 1682, 1672, 1622 and 1575 cm^{-1}, which belong to vibrations of $\rangle C{=}\overset{+}{N}\langle$, $\rangle C{=}O$, conjugated $\rangle C{=}C\langle$ bonds of the ring, and $\rangle C{-}O^{-}$ respectively [6].

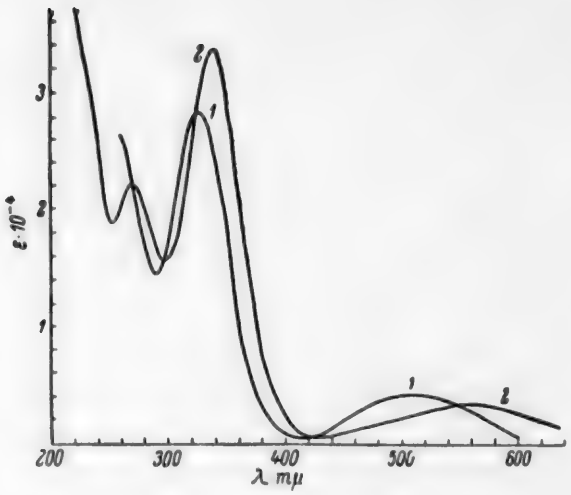


Fig. 2. Absorption spectra of solutions of 1,3-dimethyl-4-methoxy-5,6-dioxobenzimidazolone (XI). 1) In carbon tetrachloride, c 6.52 · 10^{-5} M, λ_{max} 328 and 508 mμ, λ_{min} 292 and 409 mμ; 2) in water, c 6.55 · 10^{-5} M, λ_{max} 270, 340 and 566 mμ, λ_{min} 253, 298 and 426 mμ.

The infrared spectra of the quinones (XIII) and (XI) contained intense vibration bands of the amide group of the benzimidazolone ring (1756 and 1747 cm^{-1}) and the carbonyl of an ortho-quinoid grouping (1610 and 1601 cm^{-1}) (Figs. 3 and 4). The strong fall in the latter frequency (Otting and Staiger found this band for ortho-quinones of the benzene series of 1666-1657 cm^{-1} [7]) may be explained by the presence of the NH group of the imidazolone ring in the meta-position of the benzene nucleus [8]. The same bands at 1761 and 1610 cm^{-1} are present in the spectrum of 5,6-dioxobenzimidazolone (XIV).

The spectra of the quinones (XIII) and (XI) did not contain intense bands characteristic of vibrations of $\rangle C-O^{-}$. The absorption at 1458 and 1470 cm^{-1} was caused by deformation vibrations of the C–H bonds of the CH_3 group attached to the nitrogen atom. These bands were absent from the infrared spectrum of 5,6-dioxobenzimidazolone (XVI).

The bands in the region of 1080-1250 cm^{-1} must belong to planar deformational vibrations of C–H bonds of the benzene nucleus, while the bands at 828 and 835 cm^{-1} must belong to out-of-plane vibrations [7].

Thus, the spectral data and solvatochromic properties of the quinones (XI) and (XIII) show that they exist in a polarized quinoid form without the separation of charges to the intraionoid structure of adrenochrome. This is also indicated by the capacity of compounds (XI) and (XIII) to form phenazine derivatives very readily, while this reaction is difficult with adrenochrome.

EXPERIMENTAL

2-Nitro-3,4,5-trimethoxyaniline (II). To a solution of sodium hypochlorite, which was prepared by passing chlorine (from 5.6 g of potassium permanganate and 35 ml of concentrated hydrochloric acid) into a solution of

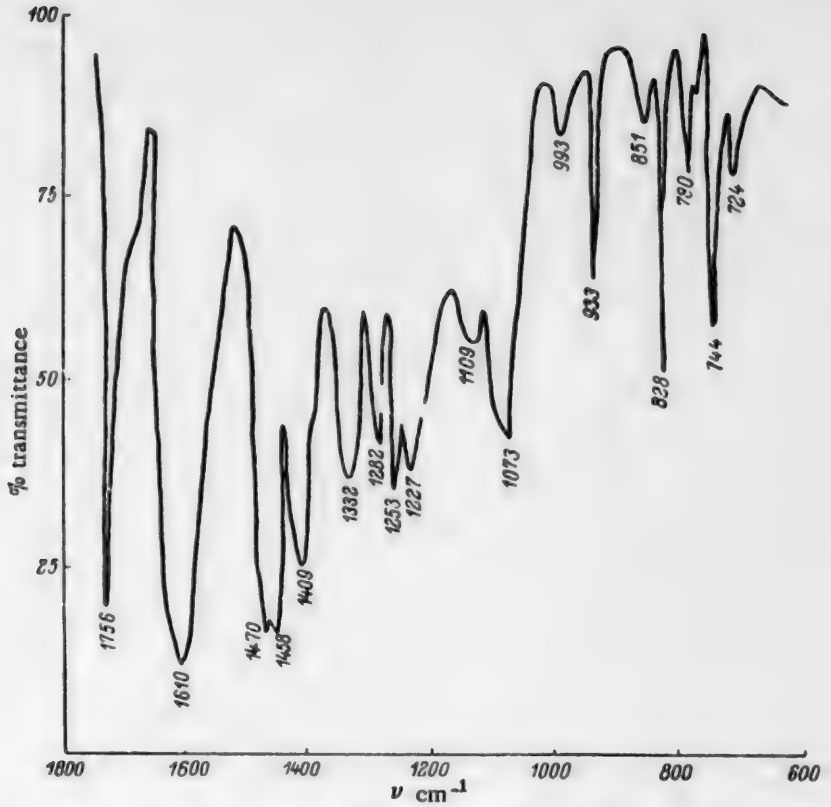


Fig. 3. Infrared spectrum of 1,3-dimethyl-5,6-dioxobenzimidazolone (XIII) in vaseline and fluorinated oils.

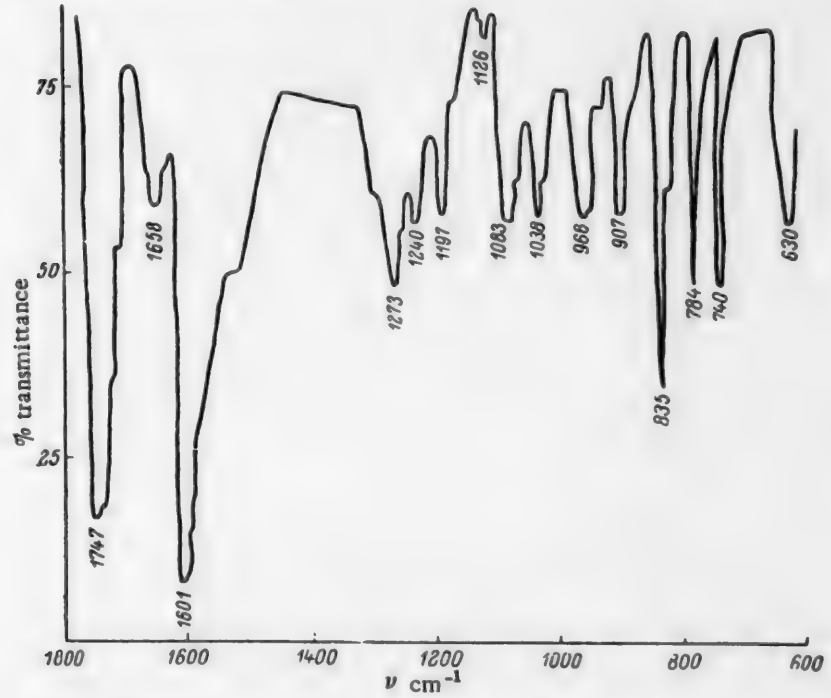


Fig. 4. Infrared spectrum of 1,3-dimethyl-4-methoxy-5,6-dioxobenzimidazolone (XI) in vaseline oil.

21 g of NaOH in 120 ml of water and 100 g of ice, was immediately added at 0° 22 g of the amide of 2-nitro-3,4,5-trimethoxybenzoic acid with m. p. 185.5° (according to literature data: m. p. 182-184° [4] and 187° [9]). The mixture was stirred for 1.5 hr while heated at a rate of ~1° per minute and then boiled under reflux for 10 min. After the mixture had cooled, the precipitate was collected and dissolved in boiling carbon tetrachloride and the residue of the unreacted amide (~1 g) discarded. The solution was evaporated and the nitroaniline precipitated with ligroin. Orangish red needles were obtained in a yield of 17 g (87%) and had m. p. 79°. According to literature data [4]: m. p. 82-83°. The substance was readily soluble in organic solvents and difficulty soluble in ligroin.

4,5,6-Trimethoxybenzofuroxane (III). A 0.7 g sample of 2-nitro-3,4,5-trimethoxyaniline was boiled for 15 min in a solution of hypochlorite prepared as described above from 1.2 g of potassium permanganate and 8 ml of hydrochloric acid. The oily drops of the amine gradually solidified and changed into a greenish yellow crystalline precipitate. After the mixture had cooled, the crystals were collected, washed with water on the filter, and recrystallized from methanol. The yield was 0.65 g (93.5%) and the m. p. 129.5°. The substance was soluble in ether and alcohols, and almost insoluble in water.

Found %: C 48.38; H 4.67; N 12.39, 12.59; OCH_3 40.30. M 218.0. $C_9H_{10}O_5N_2$. Calculated %: C 47.80; H 4.45; N 12.40; OCH_3 41.15. M 226.2.

1,2-Diamino-3,4,5-trimethoxybenzene (VI). A 17-g sample of 2-nitro-3,4,5-trimethoxyaniline was hydrogenated at room temperature and atmospheric pressure in 90 ml of alcohol over a platinum catalyst [10]. The hydrogenation proceeded readily with heat evolution by the reaction mass. After the theoretical amount of hydrogen had been absorbed, the slightly colored solution was filtered to remove the catalyst and evaporated in vacuum to yield a dark oily residue, which was condensed with urea without purification.

For identification of the diamine, 4,5,6-trimethoxyselenodiazole (IV) was prepared from it. Aqueous solutions of excess selenious acid and the diamine were mixed, the mixture heated to boiling, and the precipitate collected, washed with water, and recrystallized from ligroin with charcoal. The light yellow needles had m. p. 113-114°. The substance was readily soluble in organic solvents and crystallized from a large volume of water.

Found %: N 9.99, 9.98. $C_9H_{10}O_3N_2Se$. Calculated %: N 10.25.

4,5,6-Trimethoxybenzimidazolone (V). The crude diamine obtained by reduction of 17 g of 2-nitro-3,4,5-trimethoxyaniline was fused with 20 g of urea at 190-210° (in the bath) for 30 min. The cooled melt was dissolved in 100 ml of hot 7.5% sodium hydroxide and the solution treated with charcoal. The dark solution was made weakly alkaline by the addition of hydrochloric acid and then excess acetic acid added. The light brown precipitate which formed when the solution was cooled was collected (weight 13.7 g), recrystallized from a large volume of water with charcoal, reprecipitated twice from alkali with hydrochloric acid, and dried at 120°. The yield was 11.65 g (70%). The fine colorless crystals had m. p. 226-226.5°. The compound crystallized from alcohols and was difficulty soluble in nonpolar organic solvents.

Found %: C 54.01, 54.03; H 5.47, 5.43. $C_{10}H_{12}O_4N_2$. Calculated %: C 53.56; H 5.38.

1,3-Dimethyl-4,5,6-trimethoxybenzimidazolone (XII). To a solution of 9 g of 4,5,6-trimethoxybenzimidazolone in 100 ml of 6.5% NaOH at 85-90° was added 7.7 ml of dimethyl sulfate, the mixture stirred for 15 min, dry alkali and dimethyl sulfate added in the same amounts as before, and the mixture stirred at 90° for 15 min. The solution was evaporated to dryness, the residue extracted with benzene, and the extract dried with $MgSO_4$ and evaporated to dryness. We obtained 9.1 g (89%) of a light oil, which crystallized after a long time. For analysis, the compound was recrystallized with very large losses from a mixture of ethyl acetate and ligroin at −15° and from ligroin and then it had m. p. 76°. The substance was readily soluble in all solvents apart from ligroin.

Found %: N 11.38, 11.37. $C_{12}H_{16}O_4N_2$. Calculated %: N 11.09.

1,3-Dimethyl-4-methoxy-5,6-dioxobenzimidazolone (XI). A mixture of 0.5 g of the unpurified compound (XII) and 0.5 g of sodium nitrite was dissolved in 60 ml of water and the solution cooled with ice and stirred while 4 ml of concentrated hydrochloric acid was added. The intensely colored solution was heated on a boiling water bath for 3 min, cooled rapidly and extracted with chloroform, the extract dried with $MgSO_4$ and evaporated, and the residue recrystallized from a small volume of alcohol. We obtained 0.1 g (23%) of the quinone as coarse, dark red-bronze needles with m. p. 197.5-198°. The compound was soluble in organic solvents, destroyed instantaneously by dilute alkali solutions, and readily formed the leuco compound on reduction.

Found %: C 54.83; H 4.32, N 12.89; OCH_3 13.43. $C_{10}H_{10}O_4N_2$. Calculated %: C 54.00; H 4.54; N 12.60; OCH_3 13.98.

1,3-Dimethyl-4-methoxy-5,6-dihydroxybenzimidazolone (X). To 150 mg of the quinone (XI) in 8 ml of boiling water was added ascorbic acid in small portions until the solution was decolorized. The precipitate which formed when the solution was cooled was collected, washed with water, recrystallized from water with charcoal, and then dried in vacuum over P_2O_5. The fine colorless needles darkened slowly in air. They began to darken at ~170° and melted at ~190°.

2,3-(1',3'-Imidazolone)-4-methoxyphenazine (VII). A mixture of 120 g of the quinone (XI) and 200 mg of o-phenylenediamine was dissolved in 4 ml of boiling acetic acid. The precipitate which formed when the solution was cooled was collected and recrystallized from acetic acid. The fine yellow crystals dissolved readily in alcohol, crystallized from water, and had m.p. 215-216°.

Found %: OCH_3 10.75, 11.05. $C_{16}H_{14}O_2N_4$. Calculated %: OCH_3 10.52.

The ultraviolet spectra were plotted on an SF-4 spectrophotometer with readings taken normally at 2-m μ intervals on absorption maxima and minima.

The infrared spectra were plotted on IKS-2 and IKS-14 spectrometers with an NaCl prism with the samples as pastes in vaseline and fluorinated oils. The spectra were plotted by G.I. Semenov.

SUMMARY

1,3-dimethyl-4-methoxy-5,6-dioxobenzimidazolone was obtained from 1,3-methyl-4,5,6-trimethoxybenzimidazolone by oxidation with sodium nitrite.

LITERATURE CITED

1. A.V. El'tsov, L.S. Efros, ZhOKh 30, 3319 (1960).
2. A.V. El'tsov, L.S. Efros, ZhOKh 31, 1215 (1961).
3. A.V. El'tsov, L.S. Efros, E.N. Glibin, ZhOKh 31, 1581 (1961).
4. R. Elderfield, G. Kruger, J. Org. Ch. 17, 358 (1952).
5. N. Boyer, G. Czerniak, H. Gutowsky, H. Snyder, J. Am. Chem. Soc. 77, 4238 (1955).
6. R. Heacock, Chem. Revs. 59 181 (1959).
7. W. Ottig, G. Staiger, Ber. 88, 828 (1955).
8. L. Bellamy, The Infrared Spectra of Complex Molecules. 132 (1958).
9. C. Overmyer, J. Am. Chem. Soc. 49, 499 (1927).
10. Synth. Org. Prep. [Russian translation] 1, 357 (1949).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

CHEMICAL ACTIVITY AND STERIC ACCESSIBILITY

REACTION OF ARYLMAGNESIUM HALIDES WITH CHLORO ETHERS

I. I. Lapkin and R. G. Mukhina

Perm State University

Translated from Zhurnal Obshchei Khimii, Vol. 31, No.12,
pp. 4001-4006, December, 1961
Original article submitted January 30, 1961

The reaction of organozinc and organomagnesium compounds with α-monohalo ethers normally yields ethers [1]. However, different results are obtained, depending on the degree of substitution of the ortho-positions of the aryl radical [2]: unsubstituted and mono-ortho-substituted aryl- and naphthylmagnesium halides react with α-monochloro ethers normally, i.e., to form ethers, while the reaction of di-ortho-substituted arylmagnesium halides with ethers forms di-ortho-substituted benzyl chlorides as the main products. Only the effect of the structure of the radical in the organomagnesium compound (Grignard reagent) was examined in this work.

In the present investigation we followed the changes in the reaction produced by changes in the structure of the alkoxyl group of the chloro ethers. As subjects for investigation we used three ethers: monochloromethyl ethyl, propyl, and isopropyl ethers.

As the investigations showed (Table 1), the reaction also proceeds in two directions in these cases.

$$ArMgBr + ClCH_2OAlk \rightarrow \begin{cases} ArCH_2OAlk \\ ArCH_2Cl \end{cases}$$

An increase in the molecular weight or the degree of branching of the alkoxyl group in the ether is accompanied by a fall in the yield of halides and an increase in the yield of ethers.

A study of the reaction of arylmagnesium halides with α,β-dichlorodiethyl ether, which also proceeds in the two given directions

$$ArMgBr + CH_2ClCHClOC_2H_5 \rightarrow \begin{cases} ArCHCH_2Cl \\ \quad | \\ \quad OC_2H_5 \\ ArCHClCH_2Cl, \end{cases}$$

made it possible to establish another rule of this reaction, which is as follows: chlorinated ethers with a chlorine atom in the α-position at a secondary carbon atom are more active than ethers with a chlorine atom in the same position, but at a primary carbon atom. As a result of this, the chloride yield is reduced and the ether yield correspondingly increased (Table 2).

To determine the amount of the dichloride ($RCHClCH_2Cl$) formed in this reaction, we used Schultze's method [3], which is based on the determination of the active chlorine atom in the α-position. This method is quite suitable for this purpose: preliminary experiments showed that if the substance is heated with an alcohol solution of silver nitrate for no more than 5 min, the error connected with the gradual reaction of the reagent with a chlorine atom in a β-position is minimal (0.01-0.05%).

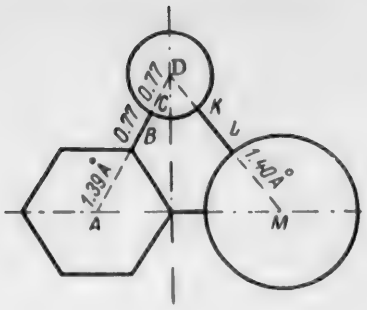
The rules found for the reaction are in complete agreement with previous conclusions on the reason for the two directions of the reaction between organo-magnesium compounds and chloro ethers, which were as follows: with an increase in the ortho-effect of the aryl radicals, groups which are less active but more accessible sterically because of smaller molecular volumes begin to react [2].

TABLE 1

ArMgBr Ar	ClCH₂OAlk Alk	Reaction Products composition: chlorine content	ArCH₂Cl	ArCH₂OAlk	Ether synthesized	Boiling point (pressure in mm)	d_4(°C)	n_D(°C)	MR_D Found	MR_D Calculated	Found % C	Found % H	Empirical Formula	Calculated % C	Calculated % H
Phenyl	Ethyl	0.32	1.1	98.9	Ethyl benzyl Ether	185°(766)	0.9433 (19°)	1.4944 (19°)	42.06	41.80	79.39	8.72	$C_9H_{12}O$	79.42	8.82
m-tolyl	The same	0.27	1.0	99.0	Ethyl m-methylbenzyl Ether	203(748)	0.9358 (18)	1.4959 (18)	46.65	46.42	79.83	9.42	$C_{10}H_{14}O$	79.96	9.39
p-tolyl	»	0.64	2.5	97.5	Ethyl p-methylbenzyl Ether	204(765)	0.9329 (18)	1.4954 (18)	46.99	46.42	79.80	9.35	$C_{10}H_{14}O$	79.96	9.39
o-tolyl	»	0.92	3.6	96.4	Ethyl o-methylbenzyl Ether	203(758)	0.9464 (17.5)	1.5000 (17.5)	46.68	46.62	80.09	9.30	$C_{10}H_{14}O$	79.96	9.39
2,5-Dimethyl-phenyl	»	1.27	5.5	94.5	Ethyl 2,5-dimethylbenzyl ether	88(10)	0.9372 (18)	1.5005 (18)	51.59	51.04	80.31	9.80	$C_{11}H_{16}O$	80.44	9.82
α-Naphthyl	»	0.17	0.8	99.2	Ethyl α-naphthylmethyl ether	134(9)	1.0488 (18.5)	1.5880 (18.5)	59.76	57.14	83.71	7.61	$C_{13}H_{14}O$	83.83	7.58
Mesityl	»	7.02	33.3	66.7	Ethyl 2,4,6-trimethylbenzyl ether	110(12)	0.9383 (17.5)	1.5031 (17.5)	56.18	55.66	80.68	10.10	$C_{12}H_{18}O$	80.85	10.18
Pentamethyl phenyl	»	15.37	85.4	14.6	Ethyl pentamethylbenzyl ether	т. пл. 26°	—	—	—	—	81.39	10.64	$C_{14}H_{22}O$	81.50	10.75
Phenyl	Propyl	0.13	0.5	99.5	Propyl benzyl ether	199(753)	0.9286 (21.5)	1.4888 (21.5)	46.67	46.62	79.78	9.31	$C_{10}H_{14}O$	79.96	9.39
m-tolyl	The same	0.15	0.6	99.4	Propyl m-methylbenzyl ether	73(6)	0.9240 (20.5)	1.4905 (20.5)	51.43	51.04	80.28	9.62	$C_{11}H_{16}O$	80.44	9.82
p-tolyl	»	0.21	0.8	99.2	Propyl p-methylbenzyl ether	77(7)	0.9209 (21)	1.4892 (21)	51.49	51.04	80.34	9.68	$C_{11}H_{16}O$	80.44	9.82
o-tolyl	»	0.30	1.2	98.8	Propyl o-methylbenzyl ether	74(6)	0.9315 (20)	1.4933 (20)	51.28	51.04	80.25	9.72	$C_{11}H_{16}O$	80.44	9.82
2.5-Dimethyl phenyl	»	0.58	2.5	97.5	Propyl 2,5-dimethylbenzyl ether	99(7)	0.9275 (20.5)	1.4953 (20.5)	56.08	55.66	80.69	10.09	$C_{12}H_{18}O$	80.85	10.18

TABLE 1. (con't)

ArMgBr Ar	ClCH₂OAlk Alk	Reaction Products: chlorine content	Reaction Products: composition ArCH₂Cl	Reaction Products: composition ArCH₂OAlk	Ether synthesized	Boiling point (pressure in mm)	d_4(°C)	n_D(°C)	MR_D Found	MR_D Calculated	Found % C	Found % H	Empirical Formula	Calculated % C	Calculated % H
3,4-Dimethyl phenyl	Propyl	0.76	3.3	96.7	Propyl 3,4-dimethylbenzyl ether	98°(7)	0.9312 (22.5°)	1.4963 (22.5°)	55.94	55.66	80.91	10.06	$C_{12}H_{18}O$	80.85	10.18
α-Naphthyl	»	0.11	0.5	99.5	Propyl α-naphthylmethyl ether	135(6)	1.0230 (22)	1.5721 (22)	64.43	61.76	83.77	7.89	$C_{14}H_{16}O$	83.96	8.05
Mesityl	»	6.04	28.7	71.3	Propyl 2,4,6-trimethyl benzyl ether	96(5)	0.9267 (22)	1.4982 (22)	60.85	60.28	81.03	10.52	$C_{13}H_{20}O$	81.20	10.48
Pentamethyl phenyl	»	12.97	71.8	28.2											
Phenyl	Isopropyl	0.10	0.4	99.6	Isopropyl benzyl ether	194(753)	0.9289 (20)	1.4850 (20)	46.35	46.42	79.81	9.27	$C_{10}H_{14}O$	79.96	9.39
m-Tolyl	The same	0.24	0.9	99.1	Isopropyl m-methylbenzyl ether	67(5)	0.9296 (20)	1.4920 (20)	51.26	51.04	80.62	9.73	$C_{11}H_{16}O$	80.44	9.82
p-Tolyl	»	0.20	0.8	99.2	Isopropyl p-methylbenzyl ether	65(5)	0.9203 (20)	1.4870 (20)	51.33	51.04	80.29	9.94	$C_{11}H_{16}O$	80.44	9.82
o-Tolyl	»	0.25	1.0	99.0	Isopropyl o-methylbenzyl ether	68(5)	0.9194 (20)	1.4848 (20)	51.17	51.04	80.20	9.78	$C_{11}H_{16}O$	80.44	9.82
2,5-Dimethyl phenyl	»	0.42	1.8	98.2	Isopropyl 2,5-dimethylbenzyl ether	83(5)	0.9248 (20)	1.4927 (20)	55.99	55.66	80.71	10.12	$C_{12}H_{18}O$	80.85	10.18
3,4-Dimethyl phenyl	»	0.62	2.7	97.3	Isopropyl 3,4-dimethylbenzyl ether	82(5)	0.9307 (20)	1.4950 (20)	55.86	55.66	80.64	10.02	$C_{12}H_{18}O$	80.85	10.18
α-Naphthyl	»	0	0	100.0	Isopropyl α-naphthylmethyl ether	125(5)	1.0265 (20)	1.5730 (20)	64.29	61.76	83.80	7.95	$C_{14}H_{16}O$	83.96	8.05
Mesityl	»	2.67	12.7	87.3	Isopropyl 2,4,6-trimethylbenzyl ether	90(5)	0.9237 (20)	1.4950 (20)	60.71	60.28	81.19	10.38	$C_{13}H_{20}O$	81.20	10.48
Pentamethyl phenyl	»	9.06	51.1	49.9			—	—							



The same conclusion follows from an examination of a plan of the arrangement of the atoms in mesitylmagnesium bromide (see figure). If the covalent radii of the magnesium (LM) and carbon atoms (CD), the radius of the aromatic ring (AB), and the length of an ordinary bond between the methyl carbon and the aromatic group (BD) are taken as 1.40, 0.77, 1.39, and 1.54 A, respectively [4], then the distance KL will equal 1.12 A and therefore, the possibility of the alkoxyl group (the diameter of the oxygen atom is 1.32 A) penetrating to the reaction center more readily than the chlorine atom (diameter 1.98 A) with some displacement of the magnesium atom from its previous position is the reason for the appearance of the second reaction product, namely, the chloride.

With an increase in the ortho-effect (which appears in the pentamethylphenyl radical because of the two methyl groups in the meta-positions, which repel the methyl groups in the ortho-positions), the access of the chloromethylene group to the reaction center is reduced to an even greater extent and the chloromethyl alkyl ether will react through its alkoxyl group with the result that chlorides become the main reaction product.

On the other hand, an increase in the molecular weight and degree of branching of the alkoxyl group must increase the yield of ether.

TABLE 2

Grignard reagent reacting with α,β-dichlorodiethyl ether (1 : 1)	Chlorine content of reaction products (%)		Composition of reaction product (%)	
	active chlorine (by Schultze's method)	total	$RCHClCH_2Cl$	$RCHCH_2Cl$ | OC_2H_5
Phenylmagnesium bromide	0.18	19.34	9.9	99.1
p-Tolylmagnesium bromide	0.26	17.88	1.4	98.6
o-Tolylmagnesium bromide	0.38	18.01	2.0	98.0
2,5-Dimethylphenylmagnesium bromide	0.39	17.41	2.2	97.8
α-Naphthylmagnesium bromide	0.40	15.22	2.5	97.5
Mesitylmagnesium bromide	1.44	16.98	8.8	91.2
Durylmagnesium bromide	2.40	17.02	15.6	84.4
Pentamethylphenylmagnesium bromide	2.98	16.82	20.6	79.4

EXPERIMENTAL

The experiments were carried out under strictly identical conditions. To an ether solution of the arylmagnesium bromide, from which the excess metallic magnesium had been removed, was slowly added an ether solution (3 volumes) of the freshly prepared chloromethyl alkyl ether with mechanical stirring and cooling of the reaction flask with iced water. The reaction mixture was heated on a water bath for 1 hr and then hydrolyzed with water and 10% acetic acid. The ether layer was separated from the aqueous layer and washed with 10% sodium carbonate solution and then with water. After the extract had been dried with anhydrous sodium sulfate, the solvent was removed, and the product wacuum distilled and then analyzed.

For determination of the chloride content, a sample of the substance was heated with an alcohol solution of silver nitrate and the amount of chloride determined from the amount of silver chloride formed, while the ether was determined by difference.

For conversion of the chloride into the ether, the reaction product was heated with a sodium alcoholate (ethylate, propylate, or isopropylate, depending on the ether present in the mixture with the chloride) and the ether obtained analyzed.

The conditions of the reaction of bromopentamethylbenzene with magnesium were described in [2].

SUMMARY

1. The study of the reaction between α-monochloro ethers and arylmagnesium halides yielding an ether $ArCH_2OAlk$ and a chloride $ArCH_2Cl$ was continued. It was established that an increase in the molecular weight or the degree of branching of the radical of the alkoxyl group in the chloro ether and the location of the chlorine atom at a secondary α-carbon atom result in a fall in the yield of the halide and an increase in the yield of the ether.

The two directions of the reaction are explained on the basis of the relation between the steric accessibility and the chemical activity of the groups of the reacting components.

2. Eighteen ethers which have not been described previously were synthesized and characterized.

LITERATURE CITED

1. A. Lieben, Lieb. Ann. 141, 136 (1867); Kessel, Lieb. Ann. 175, 44 (1875); Henry, C. r. 113, 369 (1891), J. Hamonet, Zbl. 1904, I, 1195, 1400; II, 429; 1908, 1, 1528.
2. I. I. Lapkin, O. M. Lapkina, ZhOkh 21, 108 (1951); 22, 1602 (1952).
3. G. Meyer, Analysis and Determination of the Structure of Organic Substances [Russian translation] Khar'kov (1935).
4. L. Pauling, The Nature of the Chemical Bond [Russian translation] Moscow – Leningrad GKhI (1947).

NEW METHODS OF PREPARING ESTERS AND ESTER-ACID CHLORIDES OF SELENIOUS ACID

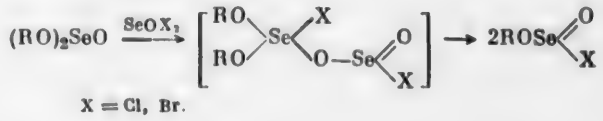
N. N. Yarovenko, M. A. Raksha, and G. B. Gazieva

Translated from Zhurnal Obshchei Khimii, Vol. 31, No.12,
pp. 4006-4010, December, 1961
Original article submitted January 19, 1961

Full esters of selenious acid are obtained by heating selenium dioxide with excess of the appropriate alcohol [1,2] and by the reaction of selenium oxychloride with alcoholates or alkali iodides with silver selenite [3]. The only ester-acid chloride of selenious acid described in the literature is the acid chloride of the ethyl ester of selenious acid [3], which was obtained by heating selenium oxychloride with alcohol.

The present work was carried out to find new methods of preparing selenium compounds from selenium oxyhalides.

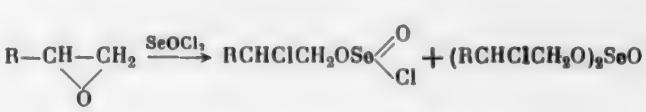
We established that full esters of selenious acid will undergo a disproportionation with selenium oxybromide and oxychloride to form ester -acid chlorides of selenious acid, apparently according to the following scheme:



$X = Cl, Br.$

In this way it was possible to obtain new ester-acid halides of selenious acid and also the first ester-acid bromides of selenious acid.

Like thionyl chloride [4], selenium oxychloride reacts with organic α -oxides to form ester-acid chlorides and full esters of selenious acid.



If the reaction mixture is stirred vigorously and cooled, the main product is an ester-acid halide of selenious acid.

In this way we obtained ester-acid chlorides and full esters of selenious acid with a chlorine atom in the alkoxyl radical from ethylene, propylene, and isobutylene oxides and epibromo- and epifluorohydrins.

The structure of the dichlorodipropyl ester of selenious acid was demonstrated by the formation of β -chloro-n-propyl alcohol in almost quantitative yield on hydrolysis of the ester. Consequently, the cleavage of α -oxides by selenium oxychloride forms ester-acid halides and full esters of selenious acid of primary alcohols.

Some ester – acid halides of selenious acid were obtained by the reaction of selenium oxyhalides both with alcoholates and directly with alcohols. In the case of pinacolyl alcohol, no acid halide of selenious acid was obtained, as selenium oxychloride shows oxidizing and chlorinating properties (elementary selenium precipitated from the reaction mixture) which could be decreased by adding the oxychloride in a complex form in analogy with the sulfonation of unsaturated compounds and acidophobic 5-membered heterocyclic systems with pyridine– sulfur trioxide by Terent'ev's method [5]. In actual fact, both selenium oxychloride and oxybromide form complex compounds with dioxane $O(CH_2CH_2)_2O \cdot SeOX_2$ very readily and in almost quantitative yield.

The composition of the complex formed is independent of the reagent ratio. The sulfur analog of selenium oxychloride, namely, thionyl chloride does not form a complex compound with dioxane [6].

The reaction of dioxane – selenyl chloride with pinacolyl alcohol yielded the pinacolyl ester of the acid chloride of selenious acid. Consequently, dioxane – selenyl chloride may be used for introducing a chloroselenyl group into organic compounds under mild conditions. Selenium oxyhalides form complex compounds with pyridine, but they are much less stable than those with dioxane.

The selenium oxychloride and oxybromide required for the reactions were obtained by the reaction of selenium with selenium dioxide and halogens.

Analogously, the reaction of selenium monobromide with selenium dioxide and chlorine yielded selenium oxychlorobromide for the first time.

$$Se_2Br_2 \xrightarrow{SeO_2 + Cl_2} SeOCl_2 + SeOBrCl$$

EXPERIMENTAL

Acid bromide of ethyl ester of selenious acid. a) In a round-bottomed flask fitted with a reflux condenser with calcium chloride tube were mixed 2.7 g (0.0143 mole) of diethyl selenite and 3.67 g (0.0144 mole) of selenium oxybromide. The mixture evolved heat. The contents of the flask were then heated for 10 min on a boiling water bath and the reaction products obtained distilled at reduced pressure. The yield was 5.5 g (86.2%) and the product had b.p. 84° at 7 mm and d_4^{20} 2.3151. The dark cherry red liquid was odorless. It dissolved readily in alcohol and ether and was hydrolyzed by water.

Found %: Br 36.34; Se 35.95. $C_2H_5O_2BrSe$. Calculated %: Br 36.40; Se 35.90.

b) Into a three-necked flask fitted with a stirrer were placed 7.89 g (0.1 g-atom) of finely ground and well-dried metallic selenium and 11.09 g (0.1 mole) of selenium dioxide and 31.97 g (0.193 mole) of bromine was added dropwise from a dropping funnel with stirring and cooling with iced water. The mixture became yellow and crystals of selenium oxybromide soon formed. The mixture was heated to 80° and kept at this temperature for 10 min to complete the reaction.

After the mixture had cooled, to the selenium oxybromide obtained in this way was added 50 ml of anhydrous alcohol and then a solution of sodium ethylate in alcohol [4.6 g (0.2 g-atom of sodium in 10 ml of alcohol] with vigorous stirring and cooling with iced water. After 30 min, the sodium bromide was removed and the filtrate distilled. The yield was 20.3 g (46%) and the product had b.p. 91° at 15 mm and d_4^{20} 2.3150.

Found %: Br 36.34; Se 35.72. $C_2H_5O_2BrSe$. Calculated %: Br 36.34; Se 35.91.

Acid chloride of ethyl ester of selenious acid. Analogously, from 3.22 g (0.0175 mole) of diethyl selenite and 2.89 g (0.0174 mole) of selenium oxychloride we obtained 5.55 g (92%) of a product with b.p. 83° at 14 mm, d_4^{20} 1.7920, n_D^{24} 1.5392. The light yellow liquid was odorless. It dissolved readily in ether and alcohol and was hydrolyzed by water.

Found %: Cl 20.72; Se 45.55. $C_2H_5O_2ClSe$. Calculated %: Cl 20.23; Se 45.01.

Acid chloride of n-butyl ester of selenious acid. Analogously, from 8.6 g (0.0352 mole) of n-dibutyl selenite and 5.8 g (0.035 mole) of selenium oxychloride we obtained 4.1 g (60.5%) of the product.

B. p. 106° at 13 mm, d_4^{20} 1.5300, n_D^{20} 1.5190.
Found %: Cl 17.14; Se 38.14. $C_4H_9O_2ClSe$. Calculated %: Cl 17.30; Se 38.90.

The light yellow liquid was odorless. It dissolved readily in ether and alcohol and was hydrolyzed by water.

Acid bromide of methyl ester of selenious acid. With continuous stirring and cooling with iced water, to a solution of 18.5 g (0.0725 mole) of selenium oxybromide in 15 ml of methanol was added a solution of sodium methylate [from 1.65 g (0.0725 g-atom) of sodium in 30 ml of methanol]. After 15-20 min, the precipitate of sodium bromide was separated and the filtrate fractionated. The yield was 7.5 g (50.7%) and the product had b.p. 87° at 15 mm and d_4^{20} 2.3568.

Found %: Br 38.37; Se 38.20. CH_3O_2BrSe. Calculated %: Br 38.33; Se 38.34.

The dark cherry red liquid was odorless. It dissolved readily in alcohol and ether and was hydrolyzed by water.

Acid chloride of methyl ester of selenious acid. From a solution of 14.4 g (0.0869 mole) of selenium oxychloride in 10 ml of methanol and 2.0 g (0.0868 g-atom) of sodium in 35 ml of methanol we obtained 5.2 g (37.1%) of the product.

B.p. 78° at 21 mm, d_4^{20} 1.7528, n_D^{20} 1.5085.
Found %: Cl 21.58; Se 48.75. CH_3O_2ClSe. Calculated %: Cl 21.98; Se 48.91.

The light yellow liquid was odorless. It dissolved readily in alcohol and ether and was hydrolyzed by water.

Acid chloride of β-chloroethyl ester and β,β'-dichlorodiethyl ester of selenious acid. Into a round-bottomed flask was placed 28.0 g (0.17 mole) of selenium oxychloride and 7.42 g (0.7 mole) of ethylene oxide bubbled into it with cooling with iced water. Heat was evolved during the reaction. The liquid obtained was left at room temperature for several hours and then distilled.

1st Fraction: b.p. 110° at 6 mm, d_4^{20} 2.0449, n_D^{20} 1.5820, 8.2 g (38%) – the acid chloride of the β-chloroethyl ester of selenious acid.

Found %: C 11.22; H 1.95; Cl 33.44; Se 37.00. $C_2H_4O_2Cl_2Se$. Calculated %: C 11.42, H 1.90; Cl 33.79; Se 37.61.

The light yellow liquid was odorless. It dissolved readily in benzene, chloroform, and carbon tetrachloride. It was hydrolyzed readily by water.

2nd Fraction: b.p. 158° at 6mm and m.p. 44° – the β,β'-dichlorodiethyl ester of selenious acid. According to literature data [7]: m.p. 44-45°.

Found %: Cl 28.58; Se 29.42. $C_4H_8O_3Cl_2Se$. Calculated %: Cl 27.95; Se 31.09.

β-Chloropropyl ester and β,β'-dichlorodipropyl ester of selenious acid. With cooling with iced water and vigorous stirring, 5.8 g (0.1 mole) of propylene oxide was slowly added dropwise to 16.6 g (0.1 mole) of selenium oxychloride. The liquid obtained was left at room temperature for several hours and then distilled.

1st Fraction: b.p. 94° at 0.5 mm, d_4^{20} 1.9058, $n^{20}D$ 1.5642, 7 g – the β-chloropropyl ester of selenious acid.

Found %: Cl 31.25; Se 35.25; $C_3H_6O_2Cl_2Se$. Calculated %: Cl 31.77; Se 35.27.

2nd Fraction: b.p. 134° at 1 mm, d_4^{20} 1.5674, n_D^{20} 1.5038, 2.6 g – the β,β'-dichlorodipropyl ester of selenious acid.

Found %: C 26.01; H 4.30; Cl 24.81; Se 28.34. $C_6H_{12}O_3Cl_2Se$. Calculated %: C 25.56; H 4.25; Cl 25.12; Se 28.05.

β-Chloropropyl alcohol. To 5.6 g (0.02 mole) of the β,β'-dichlorodipropyl ester of selenious acid was added 10.0 ml of water, the mixture left for half an hour and then saturated with potassium carbonate, and the upper layer separated and distilled. The yield was 3.6 g (98%).

B.p. 55° at 42 mm and n_D^{20} 1.4362. According to literature data [8]: b.p. 133–134°, n_D^{20} 1.4362.
Found %: Cl 37.40. C_3H_7OCl. Calculated %: Cl 37.56.

Acid chloride of β-chloroisobutyl ester of selenious acid. Under the conditions for the preparation of ester-acid halides of selenious acid, from 8.3 g (0.05 mole) of selenium oxychloride and 3.5 g of isobutylene oxide we obtained 2.0 g (18%) of the product.

B.p. 115° at 3 mm and n_D^{20} 1.5280.
Found %: C 20.34; H 3.89; Cl 29.60; Se 33.37. $C_4H_8O_2Cl_2Se$. Calculated %: C 20.17; H 3.40; Cl 29.80; Se 33.19

Acid chloride of β-chloro-γ-bromopropyl ester of selenious acid. From 16.6 g (0.1 mole) of selenium oxychloride and 13.7 g (0.1 mole) of epibromohydrin we obtained 11.6 g (33%) of the product.

B. p. 115 at 6 mm, d_4^{20} 2.1912, n_D^{20} 1.6045.
Found %: C 11.53; H 1.70; Cl 23.50; Br 26.44; Se 26.00. $C_3H_5O_2Cl_2BrSe$. Calculated %: C 11.89; H 1.65; Cl 23.43; Br 26.40; Se 26.02.

Acid chloride of γ-fluoro-β-chloropropyl ester of selenious acid. From 16.6 g (0.1 mole) of selenium oxychloride and 7.6 g (0.1 mole) of epifluorohydrin we obtained 4.3 g (18%) of the product.

B.p. 115° at 2 mm, d_4^{20} 2.0036, n_D^{20} 1.5340.

Found %: F 7.65; Cl 30.33; Se 32.13. $C_3H_5O_2FCl_2Se$. Calculated %: F 7.85; Cl 29.33; Se 32.64.

Dioxane–selenyl chloride. To 8.8 g (0.1 mole) of dioxane in 60 ml of dry carbon tetrachloride was added 16.6 g (0.1 mole) of selenium oxychloride from a dropping funnel. Each drop of selenium oxychloride produced snow white acicular crystals and weak heat evolution by the reaction mixture. The mixture was left for 1 hr and then the crystals were collected and dried in a desiccator under reduced pressure. The yield was 24.6 g (97%) and the m.p. 52°.

Found %: Cl 27.19; Se 31.48. $C_4H_8O_3Cl_2Se$. Calculated %: Cl 27.95; Se 31.09.

The substance was stable at room temperature and hydrolyzed by water to form dioxane and selenious and hydrochloric acids. It dissolved readily in diethyl ether and with difficulty in carbon tetrachloride. When heated above 150°, it decomposed to the starting components. It could be stored well in a closed vessel.

Dioxane–selenyl bromide. Analogously, from 25.48 g (0.1 mole) of selenium oxybromide and 8.8 g (0.1 mole) of dioxane we obtained 30.0 g (88%) of the product.

Found %: Br 44.78; Se 23.02. $C_4H_8O_3Br_2Se$. Calculated %: Br 46.62; Se 23.03.

The yellow acicular crystals deliquesced in air and were difficultly soluble in ether and readily soluble in dioxane.

Acid chloride of pinacolyl ester of selenious acid. To 12.7 g (0.05 mole) of dioxane–selenyl chloride was added 5.1 g (0.05 mole) of pinacolyl alcohol. The temperature of the reaction mixture fell by 15-16° and the complex dissolved. The mixture was left at room temperature for 24 hr and then heated on a water bath at 70° for 15 min. The complex dissolved completely and the liquid formed acquired a cherry red color. After being cooled to room temperature, the mixture was kept at a pressure of 20 mm until the evolution of gas bubbles ceased and then it was distilled.

1st Fraction: b.p. 100-101°, n_D^{19} 1.4218, 5.9 g–dioxane.

2nd Fraction: b.p. 90° (4 mm), d_4^{20} 1.4258, n_D^{20} 1.5102, 7.2 g (62%)–the acid chloride of the pinacolyl ester of selenious acid.

Found %: C 30.68; H 5.37; Cl 15.50; Se 34.75. $C_6H_{13}O_2ClSe$. Calculated %: C 31.10; H 5.61; Cl 15.31; Se 34.10.

The light yellow liquid was odorless. It dissolved readily in benzene, carbon tetrachloride, ether, and anhydrous alcohol. It was hydrolyzed by water.

Selenium oxychlorobromide. A mixture of 12.1 g (0.038 mole) of selenium monobromide and 8.4 g (0.076 mole) of selenium dioxide was cooled with liquid air and 8.2 g (0.23 g-atom) of chlorine added. The mixture was slowly heated to -60% and kept at this temperature for about 1 hr. It was then allowed to warm up to room temperature over a period of several hours. The liquid obtained was distilled under reduced pressure. The yield was 2.1 g (13.1%) and the product had b.p. 115° at 38 mm and d_4^{20} 3.0026.

Found %: Cl 16.51; Br 38.01; Se 38.03. OClBrSe. Calculated %: Cl 16.86; Br 38.04; Se 37.53.

The dark red liquid was odorless. It dissolved readily in ether and chloroform and was hydrolyzed by water.

SUMMARY

1. A method of preparing dioxane–selenyl halides is described.

2. New methods were found for preparing ester-acid halides of selenious acid: a) by disproportionation of full esters of selenious acid with selenium oxyhalides; b) by cleavage of organic α-oxides with selenium oxychloride; c) by the reaction of dioxane–selenyl chloride with pinacolyl alcohol.

LITERATURE CITED

1. S. Astin, A. Newman, H. Riley, J. Chem. Soc., 391 (1933).
2. N. N. Mel'nikov, M. S. Rokitskaya, ZhOKh 7, 1532 (1937).

3. A. Michaelis, B. Landmann, Lieb. Ann. 241, 156 (1887).
4. M. M. Yurchak, Kh. D. Topilyanskaya, M. S. Malinovskii, Bull. of Science Students' Conference [in Russian] Izd. L'vovsk. Univ. (1954); Pt. 2 (1955).
5. Reactions and methods of investigating organic compounds [in Russian] 2, 247 (1952).
6. Ya. L. Gol'dfarb, L. M. Smorgonskii, ZhOkh 8, 1516 (1938).
7. H. G. Cook, J. D. Tlett, B. C. Saunders, J. Chem. Soc. 1950, 3125.
8. F. Swarts, Bull. Acad. Belg. 302, 442 (1921).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

REACTION OF DIFLUOROMETHYL DIFLUOROACETATE WITH POTASSIUM FLUORIDE

N. N. Yarovenko and M. A. Raksha

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12
pp. 4011-4012, December, 1961
Original article submitted January 19, 1961

Difluoroacetic acid is used widely in the synthesis of a variety of organofluorine compounds. It was shown that mercury and silver salts of difluoroacetic acid react with iodine with heating to form difluoroiodomethane, which partly reacts with the salt of difluoroacetic acid present in the reaction mixture to form difluoromethyl difluroracetate [1].

$$(CHF_2CO_2)_2Hg \xrightarrow{I_2} CHF_2I \xrightarrow{(CHF_2CO_2)_2Hg} CHF_2CO_2CHF_2$$

It was found that difluoromethyl difluoroacetate undergoes a very interesting reaction with potassium fluoride at room temperature to form an almost quantitative yield of formyl fluoride and difluoroacetyl fluoride. Potassium difluoromethylate is evidently an intermediate product of the reaction.

$$CHF_2CO_2CHF_2 \xrightarrow{KF} [CHF_2COF + CHF_2OK] \longrightarrow CHF_2COF + HCOF + KF$$

This is a new method of preparing formyl fluoride and difluoroacetyl fluoride simultaneously.

EXPERIMENTAL

Decomposition of difluoromethyl difluoroacetate with potassium fluoride. Into a test tube, which was fitted with a gas outlet tube and a trap cooled to − 78°, were placed 9.2 g (0.063 mole) of difluoromethyl difluoroacetate [1] and 3.0 (0.058 mole) of calcined potassium fluoride. After 2-3 min there began a reaction with the evolution of gaseous products, which condensed in the trap. The liquid obtained (8.8 g) was fractionated.

1st fraction: formyl fluoride. The yield was 2.2 g (71%) and the b.p. -24.6°. Literature data [2]: b.p. -26°. Found %: C 25.4; H 2.41; F 39.58. CHOF. Calculated %: C 25.01; H 2.08; F 39.58.

2nd Fraction : difluoroacetyl fluoride. The yield was 3 g (50%) and the b.p. +2.5°.
Found %: F_{total} 58.26; $F_{anhydride}$ 19.79. C_2HOF_3. Calculated %: F_{total} 58.14; $F_{anhydride}$ 19.28.

Difluoroacetanilide. Into an ampoule containing 2.8 g (0.015 mole) of aniline was condensed 2.2 g (0.022 mole)of difluoroacetyl fluoride. The ampoule was sealed and left at room temperature for 10 hr. The white precipitate formed was separated and washed with ether. Evaporation of the ether solution yielded 0.5 g of white crystals with m.p. 56°. Literature data [3]: m.p. 58°.

Found %: N 8.34. $C_8H_7O_2NF_2$. Calculated %: N 8.19.

SUMMARY

The decomposition of difluoromethyl difluoroacetate with potassium fluoride to formyl fluoride and difluoroacetyl fluoride is described.

LITERATURE CITED

1. N. N. Yarovenko, M. A. Raksha, V. N. Shemanina, A. S. Vasil'eva, ZhOKh 27, 2246 (1947).
2. A. N. Nesmeyanov, É. I. Kan, ZhOKh 4, 1243 (1934).
3. D. Goffmann, M. Raasch, G. Rigby, P. Barriok, J. Org. Ch. 14, 747 (1949).

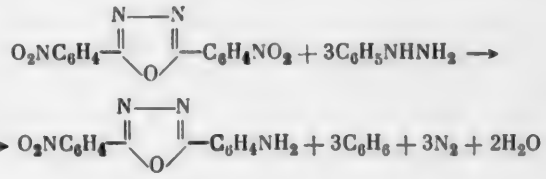
SYNTHESIS OF SOME AMINO-1,3,4-OXADIAZOLES

A. P. Grekov and V. I. Grigor'eva

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4012-4015, December, 1961
Original article submitted January 2, 1961

In previous work it was shown [1] that a nitro group in a benzene righ of 2-phenyl- and 2,5-diphenyl-1,3,4-oxadiazole is reduced readily to an amino group by phenylhydrazine.

In the present communication we describe the results of partial reduction of dinitro derivatives of 1,3,4-oxadizaole with phenylhydrazine.



As the solvent we used α-methylnaphthalene, in which the reduction of one nitro group in 2,5-di(p-nitrophenyl)- and 2,5-di(m-nitrophenyl) -1,3,4-oxadiazoles proceeded quite well. In the case of 2,5-di(o-nitrophenyl)-1,3,4-oxadiazole there was simultaneous reduction of the two nitro groups. It was also established that the nitro group is reduced readily to an amino group when the 2,5-diphenyl-1,3,4-oxadiazole molecule contains other funtional substituents and also when a phenyl radical is replaced by a pyridyl radical to form 2-(p-aminophenyl)-5- (α-pyridyl) -1,3,4-oxadiazole. However, the presence of the heterocyclic radical in the amino derivatives of 1,3,4-oxadiazole substantially worsened their preparation conditions because of the much lower chemical stability and the difficulty of isolation from the reaction mixture. We prepared derivatives of 1,3,4-oxadiazole and some hydrazides, which have not been described in the literature. In some cases the conditions for preparing dinitro derivatives of 2,5-diphenyl-1,3,4-oxadiazole were improved and their melting points determined more accurately.

EXPERIMENTAL *

2,5-Di(p-nitrophenyl)-1,3,4-oxadiazole. A mixture of 18.8 g of 1,2-di(p-nitrobenzoyl)-hydrazine and 150 ml of phosphorus oxychloride was boiled under reflux for 20 hr and then the reaction mixture was poured into water and the precipitate collected, washed with water, and recrystallized twice from dioxane and nitrobenzene. The yield was 14.7 g (83%) and the m.p. 315-315.5°. Literature data [2]: m.p. 302°.

Found %: N 18.04. $C_{14}H_8O_5N_4$. Calculated %: N 17.94.

2-(p-Aminophenyl)-5-(p-nitrophenyl)-1,3,4-oxadiazole. A mixture of 6.2 g of 2,5-di(p-nitrophenyl)-1,3,4-oxadizaole and 70 ml of α-methylnaphthalene was heated on a paraffin bath at 100-110°. To the mixture obtained was gradually added 6 ml of phenylhydrazine and the temperature of the reaction mass raised to 120-130°. The rate of the reaction was controlled by the rate of nitrogen liberation. As the reaction slowed, heating was increased and the temperature raised to 190-195°; the nitrooxadiazole dissolved completely at this point. The end of the reduction was indicated by the cessation of nitrogen evolution. On cooling, the solution deposited a brick red product, which was washed well with benzene on a filter and dried. The yield was 5.5 g (97%) and the m.p. above 300° (with decomp.). The product was very sparingly soluble in almost all organic solvents and decomposed on heating.

Found %: N 19.51. $C_{14}H_{10}O_3N_4$. Calculated %: N 19.85.

2,5-Di(m-nitrophenyl)-1,3,4-oxadiazole was obtained by boiling 22.3 g of 1,2-di(m-nitrobenzoyl)-hydrazine with 150 ml of phosphorus oxychloride for 17 hr and subsequently treating the reaction product with water. After

* R. S. Azen and L. A. Stepanenko helped with the experimental part of the work.

the product had been recrystallized several times from glacial acetic acid, the yield was 18.5 g (89%) and the m.p. 228°. Literature data [3]: m.p. 226°.

2-(m-Aminophenyl(-5-(m-nitrophenyl)-1,3,4-oxadiazole. A 10.8-g sample of 2,5-di(m-nitrophenyl)-1,3,4-oxadiazole was dissolved with heating in 60 ml of freshly distilled α-methylnaphthalene and 10.2 ml of phenylhydrazine added to the solution obtained at 100°. The temperature of the reaction mixture was first kept within the range of 100-120° and then as the rate of nitrogen evolution decreased, the temperature was raised to 160-170°. The reduction was complete after 2.5-3 hr. On cooling, the solution deposited a light brown precipitate. The yield was 6.2 g (64 %) and the m.p. 221° (from glacial acetic acid).

The yellow crystals were readily soluble in dioxane, acetone, and acetic acid.

Found %: N 19.66. $C_{14}H_{10}O_3N_4$. Calculated %: N 19.85.

1-(p-Nitrobenzoyl)-2-(p-methoxybenzoyl)-hydrazine. To a mixture of 38.4 g of p-methoxybenzhydrazine [1] and 185 ml of dry pyridine was gradually added 43.3 g of p-nitrobenzoyl chloride with vigorous stirring and then the reaction mixture was heated to 100° and poured into 850 ml of cold water. The yellow crystalline precipitate was collected, washed on the filter with water and ethanol, and recrystallized. The yield was 42.7 g (59%). After recrystallization from acetic acid, acetone, and dioxane, the product had m.p. 257°.

Found %: N 13.60. $C_{15}H_{13}O_5N_3$. Calculated %: N 13.33.

2-(p-Nitrophenyl)-5-(p-methoxyphenyl)-1,3,4-oxadiazole. A mixture of 40 g of 1-(p-nitrobenzoyl)-2-(p-methoxybenzoyl)-hydrazine and 150 ml of phosphorus oxychloride was boiled under reflux for 2 hr, by which time the precipitate was yellow-green. The reaction mixture was then cooled and poured into 1.5 liter of water and the precipitate collected, washed with water and ethanol, and recrystallized. The yield was 27.2 g (72%) and the m.p. 225-226° (from dioxane). After chromatographic purification on alumina, the product had m.p. 227-228°. The yellow crystals were readily soluble in glacial acetic acid, dioxane, and chlorobenzene and less soluble in benzene and alcohol.

Found %: N 14.42. $C_{15}H_{11}O_4N_3$. Calculated %: N 14.14.

2-(p-Aminophenyl(-5-(p-methoxyphenyl)-1,3,4-oxadiazole. A 1.5-g sample of 2-(p-nitrophenyl)-5-(p-methoxyphenyl)-1,3,4-oxadiazole was dissolved in 15 ml of α-methylnaphthalene at 140-150° and 2.5 ml of phenylhydrazine added. Vigorous reduction occurred at 175-185° and lasted for about 6 hr. On cooling, the reaction mixture deposited a precipitate. The yield was 0.83 g (62%) and the m.p. 183° (from benzene). The colorless crystals were readily soluble in acetic acid and ethanol and less so in benzene.

Found %: N 15.95. $C_{15}H_{13}O_2N_3$. Calculated %: N 15.73.

2-(p-Aminophenyl)-5-(β-pyridyl)-1,3,4-oxadiazole. A 0.67-g sample of 2-(p-nitrophenyl)-5-(β-pyridyl)-1,3,4-oxadiazole [4] was dissolved in 2.9 ml of α-methylnaphthalene at 130-140° and then the reaction mixture cooled to 100° and 2.1 ml of phenylhydrazine added to it gradually. The temperature was raised slowly to 160°. Reduction was complete when the evolution of nitrogen ceased and this usually required about 3 hr. The addition of 5 ml of benzene to the cooled reaction mixture precipitated the oxadiazole. The yield was 0.1 g (20%) and the m.p. 195° (from ethanol).

Found %: N 23.53. $C_{13}H_{10}ON_4$. Calculated %: N 23.52.

1-(p-Chlorobenzoyl)-2-(p-methoxybenzoyl)-hydrazine. To a mixture of 36.6 g of p-methoxybenzhydrazide and 175 ml of pyridine was gradually added 38.6 g of p-chlorobenzoyl chloride. The reaction mixture was then heated at 100° for 1 hr and poured into 700 ml of water. The colorless crystalline precipitate was collected, washed with water and ethanol, and recrystallized. The yield was 36.2 g (53.7%) and the m.p. 233-234° (from dioxane and glacial acetic acid).

Found %: N 11.15. $C_{15}H_{13}O_3N_2Cl$. Calculated %: N 10.92.

2-(p-Chlorophenyl)-5-(p-methoxyphenyl)-1,3,4-oxadiazole was obtained by heating 33 g of 1-(p-chlorobenzoyl)-2-(p-methoxybenzoyl)-hydrazine with 75 ml of phosphorus oxychloride for 1 hr and then pouring the reaction mixture into 500 ml of water. The colorless crystalline precipitate was collected, washed with water on the filter, recrystallized from ethanol. The yield was 27.7 g (89%) and the m. p. 165°. After chromatographic purification of a benzene solution of the oxadiazole on alumina, the product had m. p. 166°.

The colorless crystals were readily soluble in dioxane, ethanol, and benzene, sparingly soluble in ligroin, and insoluble in water.

Found %: N 9.77. $C_{15}H_{11}O_2N_2Cl$. Calculated %: N 9.76.

2,5-Di(o-aminophenyl)-1,3,4-oxadiazole. A 2.8-g sample of 2,5-di-(o-nitrophenyl) -1,3,4-oxadiazole [5] was dissolved in 9 ml of α-methylnaphthalene at 150-160° and 3.5 ml of phenylhydrazine added to the solution obtained. The reduction occurred at 90-110° in 3 hr. On cooling, the reaction mixture deposited a precipitate. The yield was 0.8 g (33%) and the m.p. 229.5-230° (from acetic acid and ethanol).

Found %: 22.35. $C_{14}H_{12}ON_4$. Calculated %: N 22.22.

SUMMARY

1. A method was developed for the partial reduction of dinitro derivatives of 1,3,4-oxadizaole. It was shown that reduction of a nitro group also occurs when the 1,3,4-oxadiazole molecule contains a pyridyl radical and also some funtional groups.

2. Seven derivatives of 1,3,4-oxadiazole and a 2-diaroylhydrazine which have not been described in the literature were synthesized and the conditions for preparing the intermediate products were improved.

LITERATURE CITED

1. A. P. Grekov, O. P. Shvaika, L. M. Egupova, ZhOKh 29, 2027 (1959); A. P. Grekov, L. N. Kulakova, O. P. Shvaika, ZhOKh 29, 3054 (1959); A. P. Grekov, O. P. Shvaika, Coll.: "Scintillators and Scintillation Materials" [in Russian] Moscow, 105 (1960); ZhOKh 30, 3804 (1960).
2. R. Stolle, A. Bombach, J. pr. Ch. (2) 74, 22 (1906).
3. R. Stolle, J. pr. Ch. (2) 137, 327 (1933).
4. A. P. Grekov, E. P. Nesynov, ZhOKh 31, 1124 (1961).
5. R. Stolle, J. pr. Ch. (2) 74, 1 (1906).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

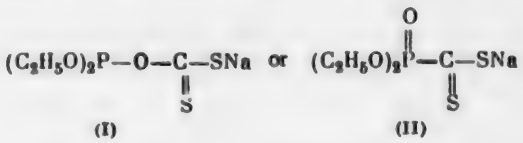
ACTION OF CARBON DISULFIDE ON SODIUM DIETHYLPHOSPHITE

B. A. Arbuzov, É. N. Dianova, and R. R. Shagidullin

A. M. Butlerov Chemical Scientific Research Institute, Kazan' State University and Kazan' Branch of the Academy of Sciences, USSR

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12
pp. 4015-4019, December, 1961
Original article submitted January 3, 1961

By the reaction of carbon disulfide and sodium diethylphosphite one might expect the formation of sodium xanthates of type (I) or (II), the action of alkyl halides on which should form the corresponding esters.



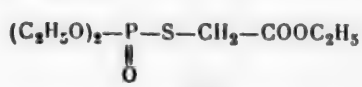
(I) (II)

In actual fact, the action of carbon disulfide on an ether solution of sodium diethylphosphite produced a reaction with the liberation of a viscous, ether-insoluble mass. However, treatment of the product obtained with methyl iodide or dimethyl sulfate yielded a compound which, according to analysis data, molecular refraction, molecular weight, and infrared spectrum (figure, a), corresponded to the O,O-diethyl S-methyl ester of thiophosphoric acid. This result was somewhat unexpected. The infrared spectrum contained an intense band of a P=O bond (ν_{max} 1259 cm^{-1}), a band at ~1330 cm^{-1} (CH_3-S-), two intense bands with maxima at 560 and 607 cm^{-1} and also a weak band at 702 cm^{-1}, which evidently belonged to P–S–(C) and (P)–S–C groupings, respectively [1], but no absorption band of a C=S bond was detected.

The results obtained were confirmed by data from experiments with ethyl bromide and diethyl sulfate: in these cases it was possible to isolate two compounds, of which one was found to be triethyl phosphate and the other, the O,O-diethyl S-ethylester of thiophosphoric acid, as was established from a comparison of the infrared spectra [1]. Thus, it was found that the formation of thiophosphoric esters from the reaction product of carbon disulfide and sodium diethylphosphite must be accompanied by elimination of the C=S group.

Even more unexpected results were obtained by treating the reaction product of sodium diethylphosphite with carbon disulfide with isobutyl bromide, acetyl bromide, and the acid chloride of diethylphosphoric acid. In all cases we isolated a substance which, in properties, Raman spectrum [2], and infrared spectrum, was identical with the O,O-diethyl S-ethyl ester of thiophosphoric acid.

When the reaction product of sodium diethylphosphite and carbon disulfide was treated with ethyl bromoacetate, thereaction proceeded analogously to the reaction with methyl iodide as we isolated a product corresponding in analytical data to compound (III), which was found to be identical with respect to infrared spectrum (figure, b) with the compound obtained by confirmatory synthesis by the action of chloroacetic ester on the sodium salt of the diethyl ester of thiophosphoric acid (figure, c).



(III)

The infrared spectra contained the frequency of a P=O group (1266 cm^{-1}), which indicates that the chloroacetic ester residue was connected to the phosphorus through sulfur and not through oxygen.

If the product from the action of carbon disulfide on sodium diethylphosphite is assigned the structure (I) and the products from treatment of it with alkyl halides, structure (IV), then the formation of the ester of thiophosphoric acid (V) should be accompanied by elimination of the CS group.

a) Infrared spectrum of the O,O-dimethyl S-methyl ester of thiophosphoric acid; b and c) infrared spectrum of the O,O-diethyl S-carbethoxymethyl ester of thiophosphoric acid.

$(C_2H_5O)_2P(=S)-S-SR$ (IV) $(C_2H_5O)_2P(=O)-SR$ (V)

There are reports in the literature on the instability of compounds similar in structure to (IV). According to the data of Yamasaki [3], compounds of type (VI) decompose on heating with the liberation of carbon disulfide.

$$(RO)_2P(=S)-S-C(=S)-OR \longrightarrow CS_2 + (RO)_3P{=}S$$

(VI)

Hoffmann, Moore, and Kagan [4] describe the formation of esters of phosphoric and thiophosphoric acids by the action of alkyl- and arylsulfonyl chlorides on triethyl phosphite.

$$3(C_2H_5O)_3P + RSO_2Cl \longrightarrow (C_2H_5O)_2P(=O)SR + C_2H_5Cl + 2(C_2H_5O)_3P{=}O.$$

In the review article of Schrader, Lorenz, and Mühlmann [5], data are given on the reaction of phosgene or thiophosgene with the ammonium salt of a dialkylmonothiophosphoric acid. The reaction proceeds with the liberation of carbon oxysulfide or carbon disulfide and tetraethyl monothiopyrophosphate. An analogous reaction between diethyl monosodium thiophosphate and phosgene was observed before the work of Schrader [6].

The data of Schrader [5] on the reaction between sodium diethylphosphite and thionyl chloride are very interesting for elucidating the reactions described in the present communication.

$$(C_2H_5O)_2PONa \xrightarrow{SOCl_2} (C_2H_5O)_2\overset{O}{\overset{\|}{P}}-SO\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 \xrightarrow{+(C_2H_5O)_2PONa}$$

$$\rightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}-S-\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 + (C_2H_5O)_2\overset{O}{\overset{\|}{P}}ONa.$$

Of particular interest is the recent work of Michalski, Modro, and Wieczorkowski [7] on the reaction of Bunte's salt with sodium diethylphosphite.

$$C_2H_5SSO_2Na + (C_2H_5O)_2PONa \rightarrow C_2H_5S\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$$

The latter reaction might, to some extent, explain the unexpected formation of the O,O-diethylS-ethyl ester of phosphoric acid by the action of isobutyl bromide, acetyl bromide, or the diacid chloride of diethylphosphoric acid on the reaction product of sodium diethylphosphite and carbon disulfide.

Another hypothesis to explain the reaction of the product from sodium diethylphosphite and carbon disulfide with various halogen derivatives is the elimination of the CS group by the action of carbon disulfide on sodium diethylphosphite with the formation of a salt of diethylthiophosphoric acid. Analysis of the mass formed by carbon disulfide and sodium diethylphosphite after it had been dried cardfully in vacuum showed that the phosphorus content of the product actually corresponded to the sodium salt of the diethyl ester of thiophosphoric acid.

However, its properties did not correspond to those of the crystalline product formed by the action of sulfur on sodium diethylphosphite.

The data presented in the communication are inadequate for determining the course of the reaction between sodium diethylphosphite and carbon disulfide and further study of this reaction is required.

EXPERIMENTAL

Reaction of sodium diethylphosphite with carbon disulfide and dimethyl sulfate. To a solution of 40 g of sodium diethylphosphite in dry ether was carefully added 24 g of carbon disulfide dropwise. A vigorous reaction occurred with the liberation of a viscous, very hygroscopic, ether-insoluble mass. To the reaction mixture was added 30.8 g of dimethyl sulfate. The viscous precipitate began to crystallize. The flask was heated on a water bath for 1 hr. After separation of the precipitate and removal of the ether, the residue was vacuum distilled. A substance with the following constants was isolated:

b.p. 71-72° (0.5 mm), d_0^{20} 1.1445, n_D^{20} 1.4577, MR_D 43.89; calcu. 43.96.
Found %: C 32.62; H 7.08; P 17.14, 17.20; S 17.19. M 181.7 (cryoscopically). $C_5H_{13}O_3PS$. Calculated %: C 32.59; H 7.11; P 16.83; S 17.40. M 184.2.

Reaction of sodium diethylphosphite with carbon disulfide and ethyl bromide. To a solution of 119 g of sodium diethylphosphite in absolute ether was added 71 g of carbon disulfide dropwise. The ether was decanted and the mass formed dissolved in absolute acetone. To the solution was added 102.5 g of ethyl bromide. Heat was evolved and a precipitate formed. After removal of the precipitate and evaporation of the acetone, the residue was vacuum distilled on a column (8 theoretical plates). Two substances with the following constants were isolated:

1st fraction: b.p. 79-80° (4 mm), d_0^{20} 1.0721, n_D^{20} 1.4118, MR_D 42.27; Calcu. 42.42.
Found %: P 17.16; 16.67. $C_6H_{15}O_4P$. Calculated %: P 17.0.

2nd fraction: b.p. 95° (4 mm), d_0^{20} 1.1105. n_D^{20} 1.4614, MR_D 49.02; Calcu. 48.57. M(cryoscopically) 199.4. $C_6H_{15}O_3PS$. Calculated: M 198.24.

Reaction of sodium diethylphosphite with carbon disulfide and isobutylbromide. From 30 g of sodium diethylphosphite, 17.7 g of carbon disulfide, and 32 g of isobutyl bromide, under the conditions described for ethyl bromide we obtained a substance with the following constants:

b.p. 96.5-97° (3.5 mm), d_0^{20} 1.0850, n_D^{20} 1.4600, MR_D 50.04; Calcu. 48.57.
Found %: C 37.89, 37.51; H 7.67; 7.83; P 15.27; 15.37; S 16.68, 16.86. M (cryoscopically) 199.37. $C_6H_{15}O_3PS$. Calculated %: C 36.34; H 7.62; P 15.63; S 16.17. M 198.24.

Reaction of sodium diethylphosphite with carbon disulfide and acetylbromide. From 119 g of sodium diethylphosphite, 71 g of carbon disulfide, and 122 g of acetyl bromide we obtained a substance with the following constants:

b.p. 106.5-107.5° (5.5 mm), d_0^{20} 1.1046, n_D^{20} 1.4563, MR_D 48.84; Calcu. 48.57.
Found %: C 36.55, 36.72; H 7.81, 7.85; P 16.13, 15.95; S 15.34, 15.52. M (cryoscopically) 198.33. $C_6H_{15}O_3PS$. Calculated %: C 36.34; H 7.62; P 15.63; S 16.17. M 198.24

Reaction of sodium diethylphosphite with carbon disulfide and the acid chloride of diethylphosphoric acid. From 119 g of sodium diethylphosphite, 71 g of carbon disulfide and 129 g of the acid chloride of diethylphosphoric acid we isolated two substances with the following constants:

1st fraction: b.p. 83-84° (7 mm), d_0^{20} 1.0678, n_D^{20} 1.4085, MR_D 42.14; Calcu. 42.42.
Found %: C 40.01, 39.86; H 8.34, 8.16; P 17.12, 16.97. $C_6H_{15}O_4P$. Calculated %: C 39.56; H 8.29; P, 17.02.
2nd fraction: b.p. 99° (7 mm), d_0^{20} 1.0928, n_D^{20} 1.4561, MR_D 49.32; Calcu. 48.57.
Found %: C 37.7, 37.59; H 7.94, 7.88; P 16.17, 16.33. M (cryoscopically) 193.23. $C_6H_{15}O_3PS$. Calculated %: C 36.34; H 7.62; P 15.63. M 198.24.

Reaction of sodium diethylphosphite with carbon disulfide and ethyl bromoacetate. From 119 g of sodium diethyl phosphite, 71 g of carbon disulfide, and 129 g of ethyl bromoacetate we obtained a substance with the following constants:

b.p. 125.5–126° (1 mm), d_0^{20} 1.1807, $n^{20}D$ 1.4621, MR_D 59.63; Calcu. 59.46.
Found %: C 38.03, 38.24; H 6.79, 6.90; P 11.89, 11.75. M (cryoscopically) 263.2. $C_8H_{17}O_5PS$. Calculated %: C 37.49; H 6.68; P 12.14. M 256.3.

Action of ethyl chlorocaetate on the sodium salt of the diethyl ester of thiophosphoric acid. To a solution of 55.5 g of the sodium salt of the diethyl ester of thiophosphoric acid in absolute ether was added 35.5 g of chloroacetic ester. Heat evolution was observed. The reaction mixture was heated on a water bath for 10 hr. After separation of the precipitate and removal of the ether, the residue was vacuum distilled. A substance with the following constants was obtained:

b.p. 127–127.5° (1.5 mm), d_0^{20} 1.1806, n_D^{20} 1.4610, MR_D 59.57; Calcu. 59.46.
Found %: P 12.52. $C_8H_{17}O_5PS$. Calculated %: P 12.10.

The infrared spectra were plotted on a UR-10 spectrophotometer. The sample was in the form of a thin film of liquid between two KBr plates.

SUMMARY

Sodium diethylphosphite reacts with carbon disulfide. The action of methyl iodide or dimethyl sulfate on the product obtained yields the O,O-diethyl S-methyl ester of thiophosphoric acid. An analogous reaction occurs with ethyl bromide or diethyl sulfate with the formation of the O,O-diethyl S-ethyl ester of thiophosphoric acid.

Treatment of the reaction product of sodium diethylphosphite and carbon disulfide with ethyl bromoacetate yielded the O,O-diethyl S-carbethoxymethyl ester of thiophosphoric acid.

The reaction with acetyl bromide or the acid chloride of diethylphosphoric acid yielded the O,O-diethyl S-ethyl ester of thiophosphoric acid.

LITERATURE CITED

1. R. A. McIvor, G. A. Grant, C. E. Hubley, Can. J. Chem. 34, 1611 (1956).
2. J. Michalski, R. Mierzecki, E. Rurarz, Roczn. chem. 30, 651 (1956).
3. T. Yamasaki, Ch. A. 49, 13887 (1955).
4. W. Hoffmann, T. Moore, B. Kagan, J. Am. Chem. Soc. 78, 6413 (1956).
5. G. Schrader, W. Lorenz, R. Mühlmann, Ang. Chem. 70, 690 (1958).
6. A. E. Arbuzov, B. A. Arbuzov, P. I. Alimov, K. V. Nikonorov, N. I. Rizpolozhenskii, O. I. Fedorova, Kazansk. fil. AN SSSR, ser. khim. nauk, No. 2,7 (1956).

7. J. Michalski, T. Modro, J. Wieczorkowski, J. Chem. Soc. 1960, 1665.

Note added in proof: When the present investigation had been completed there appeared an article [D. W. Grisley, Jr., J. Org. Chem. 26, 2544 (1961)] in which it was reported that by the reaction of sodium diisopropylphosphite with subsequent treatment with methyl iodide, it was possible to obtain the normal reaction product S-methyl diisopropoxyphosphinyldithioformate as a dark red liquid. In contrast to our conditions, the reaction was carried out in tetrahydrofuran at 2-3°.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ORGANOBORON COMPOUNDS

LXXXVII. ACTION OF DIBORANE ON ARYL DERIVATIVES OF BORON

B. M. Mikhailov and V. A. Dorokhov

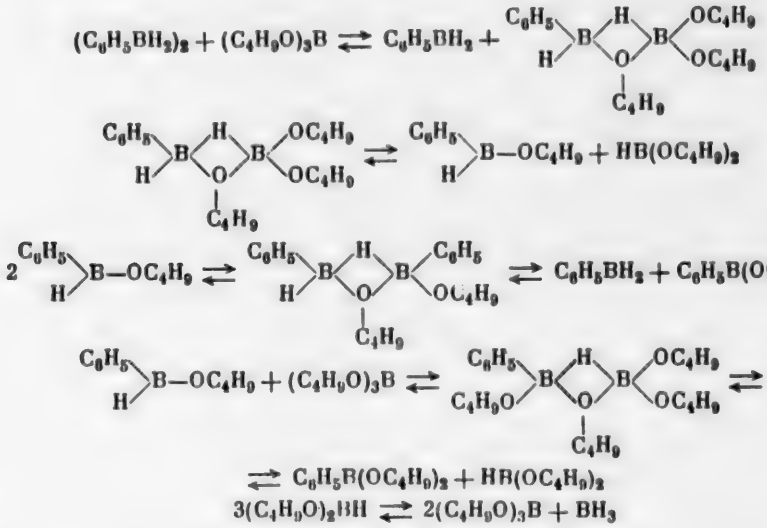
Translated from Zhurnal Obshchei Khimii, Vol 31, No 12,
pp. 4020-4023, December, 1961
Original article submitted January 6, 1961

The action of diborane on esters of aryl- and diarylboric acids is known [1,2] to form 1,2-diaryldiboranes. Diaryldiboranes are obtained in 75-80% yield from esters of diarylboric acids, but only in 40-50% yield from esters of arylboric acids with 20-25% of the starting ester inevitably recovered and this is explained by the reversibility of the reaction [1].

$$6ArB(OR)_2 + 2B_2H_6 \rightleftarrows 3(ArBH_2)_2 + 4(RO)_3B \qquad (1)$$

The equilibrium of reaction (1) cannot be displaced appreciably to the right by the use of excess diborane because of its low solubility in ether.

The reversibility of reaction (1) was demonstrated on the example of the reaction of diphenyldiborane with n-butyl borate: from an ether solution of these substances which was stirred at 30-35° for 5 hr there was liberated about 40% of diborane [calculated on equation (1)] and di-n-butyl phenylborate was obtained in 44% yield as a result of a series of successive andparallel reversible reactions.



The mechanism of the reaction examined is based on the concept that the exchange of groups between aryl and alkoxyl derivatives of boron proceeds through the formation of bridge compounds with three-center bonds formed by electron-deficient atoms [3] (B–H–B and $B-\underset{\underset{R}{|}}{O}-B$) and subsequent decomposition of the dimers in the more favorable direction energetically.

The high yield of diaryl diboranes from esters of diarylboric acids is explained by the fact that the amount of

boric ester formed in this reaction (2) is less by a factor of 4 than in the reaction of diborane with esters of arylboric acids and therefore the equilibrium is displaced to the right to a greater extent.

$$3Ar_2BOR + 2B_2H_6 \rightleftarrows 3(ArBH_2)_2 + B(OR)_3 \qquad (2)$$

In the examination of the mechanism of the reaction between esters of diarylboric acids and diborane it was assumed (1) that in the first stage there is replacement of the alkoxyl group by hydrogen and the formation of a diarylborane* and an alkoxyborane (3).

$$Ar_2BOR + {}^1/_2B_2H_6 \longrightarrow Ar_2BH + ROBH_2 \qquad (3)$$

The diarylborane then reacts with the diborane to form the diaryldiborane (4).

$$Ar_2BH + {}^1/_2B_2H_6 \longrightarrow (ArBH_2)_2 \qquad (4)$$

It seemed interesting to isolate the diarylborane formed as an intermediate compound and thus confirm the given mechanism. For this purpose, we studied the action of diborane on excess n-butyl diphenylborate. It was found that when the reaction was carried out in hexane or a very small amount of ether and the diborane passed in at a low rate, the reaction mixture soon began to deposit a crystalline precipitate, which disappeared in time. The precipitate was collected and examined and it was found to be triphenylboron and not the expected diphenylborane. Thus, diphenylborane could not be isolated, not only because of its possible conversion into diphenyldiborane, but also, apparently, because of its symmetrization into triphenylboron (5).

$$4(C_6H_5)_2BH \longrightarrow 2(C_6H_5)_3B + (C_6H_5BH_2)_2 \qquad (5)$$

The disappearance of the triphenylboron precipitate is explained by its conversion to 1,2-diphenyldiborane by diborane (6).

$$2(C_6H_5)_3B + 2B_2H_6 \longrightarrow 3(C_6H_5BH_2)_2 \qquad (6)$$

The smooth conversion of triphenylboron into diphenyldiborane by diborane in ether at room temperature was demonstrated by special experiments.

It must be assumed that the exchange of hydrogen atoms and phenyl groups between triphenylboron and diborane proceeds through the formation of a bridge compound (I) with a three-center bond B–H–B and a three-center bond B–C_6H_5–B, formed by an sp^2 orbital of the carbon atom and one hybrid sp^3 orbital from each boron atom.

$$(C_6H_5)_3B + {}^1/_2B_2H_6 \longrightarrow (C_6H_5)_2B\begin{smallmatrix}C_6H_5\\ \diagup\quad\diagdown\\ H\end{smallmatrix}BH_2 \longrightarrow (C_6H_5)_2BH + C_6H_5BH_2$$

(I)

$$(C_6H_5)_2BH + {}^1/_2B_2H_6 \longrightarrow \begin{smallmatrix}C_6H_5\\ \diagup\quad\diagdown\\ H\end{smallmatrix}B\begin{smallmatrix}C_6H_5\\ \diagup\quad\diagdown\\ H\end{smallmatrix}BH_2 \longrightarrow (C_6H_5BH_2)_2$$

In the reaction of diborane with trialkylborons there arises an analogous bridge structure (II) in which a B–R–B three-center bond is formed through an sp^3 orbital of carbon and two sp^3 orbitals of the boron atoms.

$$R_2B\begin{smallmatrix}R\\ \diagup\quad\diagdown\\ H\end{smallmatrix}BH_2$$

(II)

*In the dimeric form, tetraaryldiborane.

It was also established that diphenyldiborane is formed when diborane is passed into an ether solution of diphenylboron chloride.

EXPERIMENTAL

All operations were performed in an atmosphere of dry nitrogen.

Diborane was obtained in 60-70% yield by the dropwise addition of a 2 M ether solution of boron trifluoride etherate to a suspension of finely ground sodium borohydride in ether in an apparatus which consisted of a three-necked flask fitted with a stirrer, dropping funnel, and reflux condenser with a lead for diborane.

Reaction of 1,2-diphenyldiborane and n-butyl orthoborate. To a solution of 5.3 g (0.029 mole) of diphenyldiborane in 70 ml of absolute ether was added 9.7 g (0.042 mole) of n-butyl orthoborate. The mixture was stirred at 30-35° for 5 hr. The diborane liberated was absorbed in acetone in a Tishchenko bottle connected to the reaction apparatus. Titration of the boric acid obtained by hydrolysis of the acetone solution required 160 ml of 0.1 N NaOh solution, which corresponds to 0.008 mole of diborane. Fractional distillation of the reaction products yielded di-n-butyl phenylborate [b.p. 106-110° at 3 mm, n_D^{20} 1.4740, 5.0 g (44%)], n-butyl orthoborate, n-butyl diphenylborate, and triphenylboron.

1,2-Diphenyldiborane (from n-butyl diphenylboron and diborane in hexane). Into a three-necked flask fitted with a diborane inlet, stirrer, and reflux condenser was placed a solution of 7.6 g (0.032 mole) of n-butyl diphenylborate in 15 ml of hexane and 0.040 mole of diborane passed into it. The precipitate was collected and washed with hexane and a small amount of ether cooled to -50°. The yield was 4.6 g (80%) and the m.p. 80-83°.

Triphenylboron (from diborane and excess n-butyl diphenylborate). Into a solution of 7.6 g (0.032 mole) of n-butyl diphenylborate in 10 ml of hexane was passed about 0.003 mole of diborane. The precipitate was collected and washed with hexane. The yield was 1.1 g and the m.p. 137-145°.

Found %: B 4.22. $C_{18}H_{15}B$. Calculated %: B 4.47.

1,2-Diphenyldiborane (from diborane and triphenylboron in ether). Into a solution of 3.9 g (0.016 mole) of triphenylboron in 50 ml of ether was passed 0.022 mole of diborane. The solvent was they removed and the residue washed carefully with hexane and ether. The yield was 3.2 g (74%) and the m.p. 82-85°.

Found %: B 11.59. $C_{12}H_{14}B_2$. Calculated %: B 12.03.

1,2-Diphenyldiborane (from diphenylboron chloride and diborane). Into a solution of 4.8 g (0.024 mole) of diphenylboron chloride in 17 ml of ether was passed 0.030 mole of diborane. The solvent was removed in vacuum and the residue washed carefully with hexane and ether. The yield was 2.5 g (60%) and the m.p. 79-82°.

SUMMARY

1. 1,2-Diphenyldiborane undergoes a reversible reaction with n-butyl borate to form di-n-butyl phenylborate and diborane.

2. Triphenylboron reacts with diborane at room temperature in ether to give a high yield of 1,2-diphenyldiborane.

3. The action of diborane on diphenylboron chloride yields 1,2-diphenyldiborane.

4. Diphenylborane symmetrizes at room temperature to triphenylboron and diphenyldiborane and therefore it cannot be obtained by the action of diborane on di- and triphenyl derivatives of boron.

LITERATURE CITED

1. B. M. Mikhailov, V. A. Dorokhov, DAN SSSR 130, 782 (1960).
2. B. M. Mikhailov, V. A. Dorokhov, DAN SSSR 133, 119 (1960).
3. E. Eberhardt, B. Crawford, W. Lipscomb, J. Chem. Phys. 22, 989 (1954).

STERIC HINDRANCE AND REACTIVITY OF ORGANIC COMPOUNDS

III. ISOMERIZATION OF 1,8-DIHALONAPHTHALENES IN THE PRESENCE OF ANHYDROUS β-NAPHTHALENESULFONIC ACID

V. A. Koptyug, V. G Shubin, and V. A. Plakhov

Novosibirsk Institute of Organic Chemistry, Siberian Division of the Academy of Sciences USSR and D. I. Mendeleev Moscow Chemicotechnological Institute

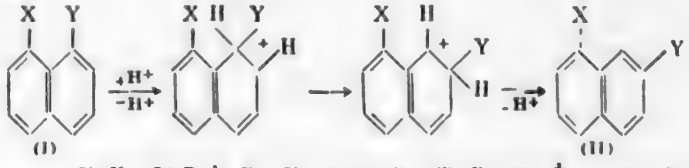
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4023-4028, December, 1961
Original article submitted January 2, 1961

When heated with hydrochloric acid (200-220°) or anhydrous β-naphthalenesulfonic acid (~110°), alkyl 1-chloronaphthyl-8 sulfones (Ia) isomerize into alkyl 1-chloronaphthyl-7 sulfones (IIa) as a result of migration of the alkylsulfonyl group [1]. Other isomeric alkyl chloronaphthyl sulfones and also unsubstituted methyl naphthyl-1 sulfones are unchanged under similar conditions. This indicates that the high reactivity of 1,8-isomers is associated with steric hindrance to the normal disposition of the peri-substituents in their molecules.

Undoubtedly this is also the reason for the migration of the chlorine atom in 1,8-dichloronaphthalene when the latter is heated with hydrochloric acid to 290° [2]. However, in this case the final product is not 1,7-dichloronaphthalene, which might have been expected, but the 1,5-isomer. This conversion evidently proceeds through the successive addition and elimination of hydrogen chloride and consequently is connected to some extent with the specific action of the latter.

In this connection it seemed interesting to study the behavior of 1,8-dihalonaphthalenes in the presence of anhydrous β-naphthalenesulfonic acid.

It was found that 1,8-dibromonaphthalene (Ib) isomerizes to 1,7-dibromonaphthalene (IIb) when heated with anhydrous β-naphthalenesulfonic acid at 110° (experiment 1). An analogous conversion occurred with 1-chloro-8-bromonaphthalene (Ic), which was isomerized into 1-chloro-7-bromonaphthalene (IIc) (experiment 2). These results show that under the given conditions, the isomerization of 1,8-dihalonaphthalenes proceeds by the normal mechanism for intramolecular isomerization of naphthalene derivatives [3], resulting in the transfer of a halogen atom to a neighboring carbon atom.



(I) (II)

a) X = Cl, Y = SO_3R; b) X = Y = Br; c) X = Cl, Y = Br; d) X = Y = Cl

1,7-Dibromonaphthalene, in which the bromine atoms are not prevented from lying in the plane of the naphthalene nucleus by steric hindrance, is not changed by heating with anhydrous β-naphthalenesulfonic acid. Thus, the isomerization of 1,8-dihalonaphthalenes under the given conditions is an irreversible process.

To compare the tendencies of different 1,8-dihalonaphthalenes to isomerize, we carried out a series of experiments in which the reaction time was insufficient for the complete conversion of the starting 1,8-isomers. The qualitative and quantitative composition of the reaction products thus obtained was determined by means of infrared spectra (see table). A comparison of the results (experiments 4-6) shows that the rate of isomerization of 1,8-dihalonaphthalenes increases in the series: 1,8-dichloronaphthalene < 1-chloro-8-bromonaphthalene < 1,8-dibromonaphthalene. This sequence is evidently the result of the fact that under otherwise equal conditions, aromatic bromo derivatives isomerize more readily than chloro derivatives. This also explains the fact that the main product from the isomerization of 1-chloro-8-bromonaphthalene is 1-chloro-7-bromonaphthalene and not 2-chloro-8-bromonaphthalene.

Isomerization of 1,8-Dihalonaphthalenes in the Presence of β-$C_{10}H_7SO_3H$ at 110°

Starting 1,8-dihalonaphthalene (I)	Experiment No.	Duration (hr)	Yield (wt%)	Composition of reaction product (in %)			
				1-X-8-Y-$C_{10}H_6$	1-X-7-Y-$C_{10}H_6$	decomposition product β-$C_{10}H_7SO_3H$	unknown compounds (by difference)
X = Y = Br	3	1	86	34	34	4	28
	4	5	86	11	60	4	25
X = Cl, Y = Br	5	5	96	22	54	4	20•
X = Y = Cl	6	5	87	83	5	4	8
	7	60	95	38	43	11	8

• According to infrared spectral data, the isomerization product of 1-chloro-8-bromonaphthalene also contained not more than 4-5% of 2-chloro-8-bromonaphthalene.

The increase in stress in the molecule of the starting compound produced when chlorine atoms are replaced by bromine atoms also has a definite effect, illustrated by the high rate of isomerization of 1,8-dibromonaphthalene as compared with 1-chloro-8-bromonaphthalene.

In addition to the starting 1,8-isomers and the corresponding isomerization products, the mixtures obtained by heating 1,8-dihalonaphthalenes with β-naphthalenesulfonic acid and removing the latter by washing with alkali also contained from 12 to 32% of components of unknown composition and structure. By means of infrared spectra, we found that they contained, in particular, a decomposition product of β-naphthalenesulfonic acid (cf. [4]) which could be obtained by heating the sulfonic acid itself in the absence of dihalonaphthalenes. There is the possibility that the sulfonic acid participated in the formation of the other by-products.

EXPERIMENTAL

1,8-Dichloronaphthalene (m.p. 85.5-87°, according to data in [5]: m.p. 89-89.5°) and 1-chloro-8-bromonaphthalene (m.p. 96.5-97°) were obtained from 1-chloro-8-naphthylamine [6] by procedures in [7] and [6], respectively.

1,8-Dibromonaphthalene was synthesized from 1,8-naphthylenediamine [8] and had m.p. 108-109°; according to data in [5]: m.p. 109-110°.

β-Naphthalenesulfonic acid was prepared as the trihydrate by the procedure in [9]. Two molecules of water of hydration were removed by keeping the trihydrate in vacuum over calcium chloride [10]. The monohydrate obtained had m.p. 119-121°; according to literature data [5]: m.p. 125.9°.

Isomerization of 1,8-dihalonaphthalenes. In all isomerization experiments the molar ratio of 1,8-dihalonaphthalenes and β-naphthalenesulfonic acid was 1 : 6.5.

The β-naphthalenesulfonic acid monohydrate was dehydrated by heating for 1.5 hr at 110° and 2 mm in a flask, which was connected to a vacuum pump through a trap filled with magnesium perchlorate. The loss in weight corresponded to the complete removal of the water of hydration. Then the appropriate 1,8-dihalonaphthalene was added to the anhydrous β-naphthalenesulfonic acid and the mixture kept in the closed flask for a definite time with a bath temperature of 110°. The reaction mixture was treated with 5% alkali solution and the reaction product extracted with ether. The yield was 86-96%.

Experiment 1. 1,8-Dibromonaphthalene was heated with β-naphthalenesulfonic acid for 5 hr. The reaction product was pressed on a porous plate and recrystallized, when it had m.p. 74-75° (from alcohol).

Found %: C 42.3, 42.5; H 2.23, 2.25. $C_{10}H_6Br_2$. Calculated %: C 42.0; H 2.10.

A mixture of the substance obtained with the starting 1,8-dibromonaphthalene melted at 60°, while the melting point of a mixture with 1,7-dibromonaphthalene (m.p. 74.5-75.5°) was not depressed.

Experiment 2. When the reaction mixture was heated for 15 hr, 1-chloro-8-bromonaphthalene gave a product with m.p. 62-63° (from alcohol).

Found %: C 50.3, 50.4; H 2.68, 2.76. $C_{10}H_6ClBr$. Calculated %: C 49.7; H 2.55.

A mixture of the substance obtained with the starting 1-chloro-7-bromonaphthalene (m.p. 65.0-65.5°) was not depressed. The ultraviolet absorption spectra of the substance isolated and 1-chloro-7-bromonaphthalene were also found to be identical.

Experiments 3-7 were carried out with the same molar ratio of 1,8-dihalonaphthalene and sulfonic acid under the conditions given in the table; the results of analysis of the reaction products by infrared spectra are also given in the table.

Experiment 8. 1,7-Dibromonaphthalene was heated with β-naphthalenesulfonic acid for 5 hr. The infrared spectrum of the reaction product was identical with that of the starting compound.

Analysis of isomerization products of 1,8-dihalonaphthalenes by infrared spectra. In all cases, the infrared spectra were plotted on an IKS-14 double-beam spectrophotometer with 2% solutions in CCl_4 and a layer thickness of 1 mm. The concentrations of the individual compounds in the isomerization products were determined from previously constructed calibration curves with the optical density calculated by the base-line method.

An examination of the infrared spectra of the reaction products obtained in experiments 3-7 showed that they all contained the corresponding 1,7-isomer in addition to the starting 1,8-dihalonaphthalene. In the case of 1-chloro-8-bromonaphthalene, in the spectrum of the isomerization product we detected only bands of one of the two possible 1,7-isomers, namely, 1-chloro-7-bromonaphthalene.

The infrared spectra of all the reaction products also contained additional absorption bands (476, 511, 548 572, 609 cm^{-1} and others in the region of 800-2000 cm^{-1}), which were absent from the spectra of the corresponding 1,8- and 1,7-dihalonaphthalenes and belonged to the decomposition product of β-naphthalenesulfonic acid, which was used as the catalyst. In actual fact, heating anhydrous β-naphthalenesulfonic acid at 110° for 5 hr gave ~0.5% yield of a solid substance which was insoluble in aqueous alkali and whose infrared spectrum (Fig. 1) contained these absorption bands.

For quantitative analysis of the reaction products, we used the following absorption bands: 1,8-dibromonaphthalene – 566 cm^{-1}; 1,7-isomer – 599 and 620 cm^{-1}; 1-chloro-8-bromonaphthalene – 571 cm^{-1}; 1-chloro-7-bromonaphthalene – 603 cm^{-1}; 1,8-dichloronaphthalene – 577 cm^{-1}; 1,7-isomer – 631 cm^{-1}. To eliminate the effect of absorption of the decomposition product of the sulfonic acid on the analysis result, the content of the 1,8- and 1,7-dihalonaphthalenes was determined by the difference method [11]. First of all, the content of the decomposition product of β-naphthalenesulfonic acid in all the reaction products was determined by the usual method from the bands at 511 and 609 cm^{-1}. Then the difference spectra of the reaction products relative to the decomposition product of the sulfonic acid were plotted. From these spectra we determined the content of the 1,8- and 1,7-dihalonaphthalenes. The accuracy of the analysis results was checked by plotting difference spectra with a solution of an artificial mixture of the 1,8-dihalonaphthalene, the 1,7-isomer, and the decomposition product of the sulfonic acid, prepared in accordance with the analysis results, in the comparison beam. The accuracy of the compensation for the absorption of the given component indicated the accuracy of the analysis.

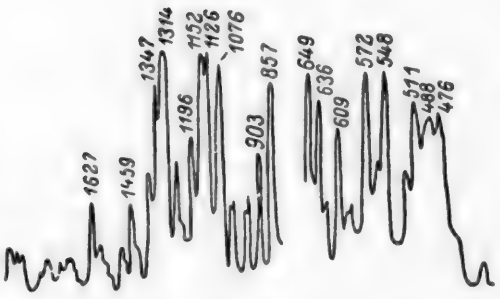


Fig 1. Infrared spectrum of decomposition product of β-naphthalenesulfonic acid.

In the difference spectrum of the isomerization product of 1-chloro-8-bromonaphthalene there appeared an absorption band at 1083 cm^{-1}, which is characteristic of 2-chloro-8-bromonaphthalene. The low intensity of the band showed that the content of this isomer in the reaction product was very low; even if it was assumed that the absorption at 1083 cm^{-1} was solely caused by 2-chloro-8-bromonaphthalene, its content could not exceed 4-5%.

As an example, Fig. 2 gives the infrared spectra for the analysis of the isomerization products of 1,8-dichloronaphthalene.

Preparation of compounds formed by isomerization of 1,8-dihalonaphthalenes. 1,7-Dichloronaphthalene was obtained from 2-chloronaphthalene-8-sulfonyl chloride [12] by the procedure in [13]. It had m.p. 62.5-63°. Literature data [5]: 63.5-64.5° [5].

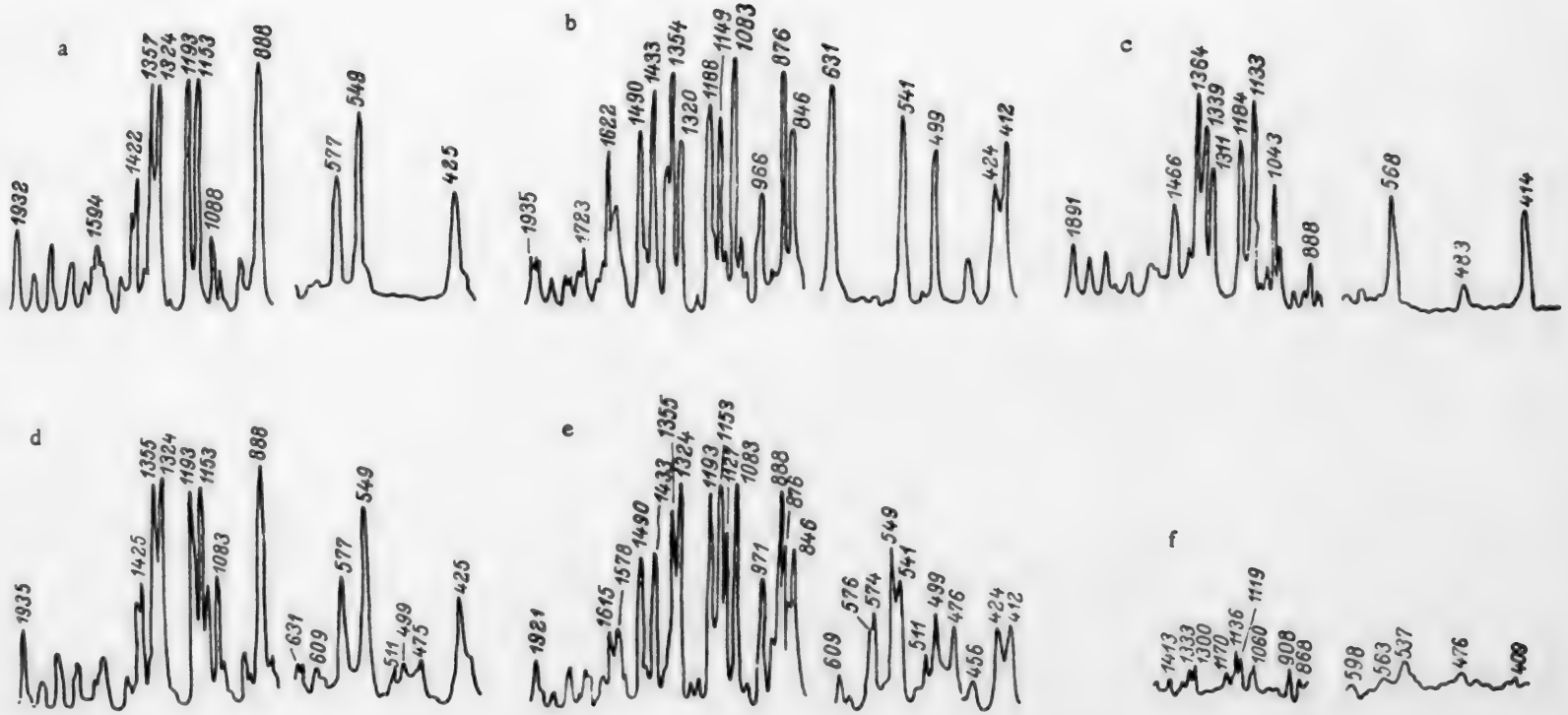


Fig. 2. Infrared spectra: a) 1,8-dichloronaphthalene; b) 1,7-dichloronaphthalene; c) 1,5-dichloronaphthalene; d) isomerization product of 1,8-dichloronaphthalene (reaction time 5 hr, experiment 6); e) the same (reaction time 60 hr, experiment 7) ; f) difference spectrum (experiment 7).

1-Chloro-7-bromonaphthalene. A suspension of 6.3 g of 2-bromo-8-naphthylamine hydrochloride [14] in 140 ml of water and 53 ml of concentrated hydrochloric acid was diazotized at 0° with a solution of 1.7 g of $NaNO_2$. The solution of the diazo compound was added to a cooled solution of cuprous chloride (from 6.3 g of copper sulfate) in 100 ml of concentrated hydrochloric acid. The reaction mixture was slowly heated to 40° and then to boiling. Steam distillation yielded 3.8 g of product with m.p. 65-65.5° (from alcohol). Literature data [15]: m.p. 68-68.5°.

Found %: C 50.3; H 2.76. $C_{10}H_6ClBr$. Calculated %: C 49.7; H 2.55.

2-Chloro-8-bromonaphthalene was obtained by bromination of 2-chloronaphthalene [16] and purified by recrystallization from alcohol; it had m.p. 67.5-68°. Literature data [5]: m.p. 68-69°.

1,7-Dibromonaphthalene was synthesized by bromination of 2-bromonaphthalene analogously to the preparation of 2-chloro-8-bromonaphthalene (cf. [17]). It had m.p. 74.5-75.5° (from alcohol); according to data in [5]: m.p. 75°.

SUMMARY

When 1,8-dihalonaphthalenes (halogen = Cl or Br) are heated with anhydrous β-naphthalenesulfonic acid at 110°, there is irreversible migration of one of the halogens to the neighboring β-position. The isomerization rate increases in the series: 1,8-dichloronaphthalene < 1-chloro-8-bromonaphthalene < 1,8-dibromonaphthalene.

LITERATURE CITED

1. V. A. Koptyug, T. N. Gerasimova, N. N. Vorozhtsov Jr., ZhOKh 30, 612 (1960).
2. H. E. Armstrong, W. P. Wynne, Chem. News 76, 69 (1897); Proc. Chem. Soc. 182, 154 (1896/97).
3. N. N. Vorozhtsov Jr., V. A. Koptyug, ZhOKh 28, 372 (1958); ZhOKh 30, 999 (1960).
4. H. Kuczynski, L. Kuczynski, E. Sucharda, Ročzn. Chem. 18, 625 (1938).
5. Elsevier's Enc. Org. Chem., Ser. III, 12B.
6. J. Cason, J. D. Wordie, J. Org. Ch. 15, 617 (1950).
7. E. Bergmann, J. Hirschberg, J. Chem. Soc. 1936, 331.
8. H. H. Hodgson, J. S. Whitehurst, J. Chem. Soc. 1947, 80.
9. Houben-Weyl, Methoden der organischen Chemie, 4 Aufl., IX, 456 (1955).
10. O. N. Witt, Ber. 48, 757 (1915).
11. V. A. Koptyug, T. N. Gerasimova, V. A. Plakhov, ZhOKh 31, 1611 (1961).
12. E. H. Huntress, F. H. Carten, J. Am. Chem. Soc. 62, 511 (1940).
13. R. W. Beattie, F. C. Whitmore, J. Am. Chem. Soc. 55, 1546 (1933).
14. N. J. Leonard, A. M. Hyson, J. Am. Chem. Soc. 71, 1392 (1949).
15. M. M. Dashevskii, G. P. Petrenko, ZhOKh 25, 1378 (1955).
16. J. Guareschi, Jahresber. 1888, 1921.
17. H. E. Armstrong, Rossiter, Chem. News 65, 58 (1892).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

POLYETHYLENE GLYCOLS AND SOME OF THEIR DERIVATIVES

A. N. Pudovik and T. M. Moshkina

Kazan' Branch of the Motion Picture Scientific Research Institute

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12
pp. 4028-4033, December, 1961
Original article submitted December 26, 1960

The purpose of the present work was the synthesis of individual polyethylene glycols, the study of their properties, and the preparation from them of mono- and diphosphates and also esters of monochloroacetic acid. It was surmised that these compounds might be of interest and find application as surface-active substances, tanning agents, and plasticizers in the production of motion picture materials.

Tetra- and hexa-ethylene glycols were prepared by condensation of the monosodium salt of ethylene or diethylene glycol with β,β'-dichlorodiethyl ether [1]. The chain was built up further by the action of the monopotassium glycolates of various polyethylene glycols on the dichlorohydrins of polyethylene glycols. In this way we obtained a series of polyethylene glycols with the general formula: $HO(CH_2CH_2O)n\ H$, where n = 4,6,8,14,18,22,42,90,186; and molecular weights from 200 to 8,000 and studied their properties (Table 1).

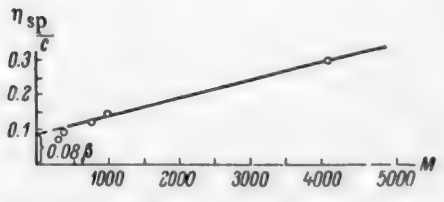
To confirm the structure of the individual polyethylene glycols, we determined their hydroxyl group contents by the Chugaev–Tserevitinov and Verley methods. The molecular weights of the low-molecular polyethylene glycols were determined cryoscopically. The relative viscosity of dilute solutions in dry dioxane at 20° was measured and the data obtained used to determine the intrinsic viscosity.

The individual polyethylene glycols were used for the synthesis of mixed phosphoric esters. Polyethylene glycol mono- and diphosphates were obtained by the action of the acid chloride of diethylphosphoric acid on the appropriate polyethylene glycols.

$$(C_2H_5O)_2POCl + HO(CH_2CH_2O)_nH \xrightarrow{(C_2H_5)_3N} \begin{cases} \rightarrow (C_2H_5O)_2\overset{\overset{O}{\|}}{P}O(CH_2CH_2O)_nH \quad (I) \\ \rightarrow (C_2H_5O)_2\overset{\overset{O}{\|}}{P}O(CH_2CH_2O)_n\overset{\overset{O}{\|}}{P}(OC_2H_5)_2 \quad (II) \end{cases}$$

(I): $n = 1, 2, 4, 6, 14, 18, 90$; (II): $n = 4, 8, 42$.

Depending on the ratio of diethyl chlorophosphate to polyethylene glycol, either mono- (I) or diphosphates (II) were obtained predominantly. The monophosphate (I) was purified by distillation in normal or high vacuum (at $n < 6$) or by fractional precipitation (at $n > 6$). The esters (I) and (II) hardly differed in external appearance from the starting polyethylene glycols. They dissolved readily in water, alcohol, dioxane, benzene, anisole, and other solvents.



Relation of intrinsic viscosity to molecular weight of polyethylene glycol monophosphates in dioxane at 20°.

The preparation of pure phosphoric esters (I) and (II) of high molecular weight involved considerable difficulties as their solubilities and other physical properties become very similar to those of the starting polyethylene glycols. The characteristics of (I) are given in Table 2.

The molecular weights of the polyethylene glycol monophosphates were determined cryoscopically. This method was used by Staudinger [2] to determine the mean molecular weights of polyethylene glycol fractions with molecular weights up to 12,000. In this work it was shown that in the determination of the molecular weights of polyethylene glycols and their phosphorus derivatives by this method, reliable results can be obtained for polymers with molecular weights no higher than 1500-

TABLE 1. Polyethylene Glycols $HO(CH_2CH_2O)nH$

No.	n	External appearance of product	Solubility	Yield	Boiling (pressure in mm) or melting point	% OH		M		Intrinsic viscosity η_{sp}/c
						Found	Calculated	found cryscopically	Calcu.	
1	4	Yellow liquid	Soluble in ether, alcohol, benzene, dioxane, anisole, and water	57	195° (12)	17.43	17.57	—	—	—
2	6	The same	The same	45	245 (12)	11.55	12.05	279	282	0.03
3	8	Viscous yellow liquid	—	—	230 (0.01)	9.60	9.18	346, 350	370	—
4	14	Very viscous liquid which could not be distilled in high vacuum	Slight solubility in ether. Soluble in other solvents	—	—	5.44	5.36	615	634	0.16
5	18	Yellow, vaseline-like mass	The same	50	—	4.12, 4.20	4.19	830, 790	810	0.17
6	22	The same	" "	—	—	3.54	3.50	940, 935	986	—
7	42	White powder	Insoluble in ether, soluble in other solvents	43	M.p. 30—34	2.10	1.81	—	—	0.22
8	90	The same	The same	57	M.p. 36—40	—	—	—	—	0.33
9	186	" "	" "	22	M.p. 42—45	—	—	—	—	0.52

TABLE 2. Polyethylene Glycol Monophosphates $(C_2H_5O)_2\overset{O}{\overset{\|}{P}}\text{-}O(CH_2CH_2O)nH$

No.	n	External appearance of Product	Yield (%)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		% P		Intrinsic viscosity η_{sp}/c
							Found	Calcu.	Found	Calcu.	
1	2	Yellow liquid	73	179—183° (12)	1.4222	1.1370	54.06	54.81	13.54	12.80	—
2	4	The same	40	135—140 ($5 \cdot 10^{-3}$)	1.4480	1.1410	77.43	76.58	9.21	9.40	0.06
3	6	" "	40	175—180 ($9 \cdot 10^{-3}$)	1.4492	1.1350	98.72	98.33	7.40	7.50	0.10
4	14	Vaseline-like mass	55	—	—	—	—	—	6.80	6.73	0.12
5	18	The same	—	—	—	—	—	—	3.34	3.27	0.14
6	90	White powder	30	M.p. 36—40	—	—	—	—	0.58	0.75	0.28

1600. For polymers with a higher molecular weight the depression of freezing point of dioxane solutions became very small (less than 0.01°) and slight errors in its determination could lead to inaccurate values for the molecular weights.

For a series of polyethylene glycol monophosphates with n = 6, 14, 18, and 90, we measured the relative viscosity of dilute solutions of them in dioxane at 20° and used the data obtained to calculate the constants K_m and β in the modified Staudinger equation: $\frac{\eta_{sp.}}{c} = K_m \cdot M + \beta$. The values obtained were as follows: $K_m = 0.49 \cdot 10^{-4}$ and β = 0.08 (see figure). These constants may be used to determine the molecular weights of polyethylene glycol monophosphates viscosimetrically.

The individual polyethylene glycols were also used for the synthesis of mono- and di(chloroacetates) of polyethylene glycols. These were obtained by the action of chloroacetyl chloride on the polyethylene glycols.

$$ClCH_2COCl + HO(CH_2CH_2O)_nH \rightarrow \begin{cases} ClCH_2COO(CH_2CH_2O)_nH \ (III) \\ ClCH_2COO(CH_2CH_2O)_nCOCH_2Cl \ (IV) \end{cases}$$

(III): n = 3, 6; IV: n = 2, 3, 14, 18.

The lower members of these series were sparingly soluble in water; with an increase in the number of ethyleneoxy groups in the molecule, their solubility gradually increased. Thus, hexaethylene glycol mono(chloroacetate) was appreciably soluble in water. The chloroacetates (III) and (IV) were soluble in aqueous alcohol (1 : 3) and in most organic solvents. The characteristics of (III) and (IV) are given in Table 3.

TABLE 3

No	n	External appearance of product	Yield %	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calcu	% Cl Found	% Cl Calcu
Polyethylene glycol monochloroacetates $ClCH_2COO(CH_2CH_2O)_nH$										
1	3	Yellow liquid	56	210—212° (10)	1.4632	1.203	46.24	45.7	15.90, 15.55	15.7
2	8	Viscous yellow liquid, which could not be distilled in high vacuum	44	—	1.4688	1.187	83.81	83.17	10.23, 10.20	9.9
Polyethylene glycol dichloroacetates $ClCH_2COO(CH_2CH_2O)_nCOCH_2Cl$										
1	2	Yellow liquid	59	192 (10)	1.4752	1.358	53.47	53.84	—	—
2	3	The same	18	215 (10)	1.4720	1.314	64.56	64.67	23.40, 23.56	23.4
3	14	Very viscous liquid	50	—	—	—	—	—	9.48, 9.59	9.1
4	18	Vaseline-like oil	51	—	—	—	—	—	7.52, 7.50	7.3

EXPERIMENTAL

The polyethylene glycols were prepared by the procedure described in [1]. The polyethylene glycols with n < 8 were purified by vacuum distillation and those with n > 8, by precipitation from benzene with ether.

Polyethylene glycol monophosphates (Table 2). To a solution of the polyethylene glycol in ether was added triethylamine and then an equimolecular amount of the acid chloride of the diethyl ester of phosphoric acid was introduced slowly with vigorous stirring and cooling to 0°. Stirring was continued for a further 1 hr. The precipitate of triethylamine hydrochloride was removed by filtration and the ether distilled from the filtrate on a water bath.

Depending on the molecular weight of the polyethylene glycol monophosphate obtained, the residue was then treated by one of two methods: low-molecular products were distilled in normal or high vacuum and those with a molecular weight of more than 500 were isolated from an ether solution by cooling, recrystallized, and dried to constant weight.

Tetraethyl tetraethylene glycol diphosphate. With cooling and stirring, 35.4 g of diethyl chlorophosphate was added dropwise to a mixture of 20 g of tetraethylene glycol and 11.3 g of triethylamine in 100 ml of absolute ether. The mixture was stirred at 25-30° for 1 hr. The precipitate of triethylamine hydrochloride was removed. The ether, triethylamine, and unreacted starting materials were removed by vacuum distillation. The residue was dissolved in 3-4 times the amount of anhydrous alcohol and the solution heated for 3-4 hr with freshly calcined alumina. After removal of the alumina, activated charcoal was added to the filtrate and heating continued for a further 2 hr. The charcoal was removed by filtration and the alcohol distilled from the filtrate in vacuum with gentle heating. The viscous yellow liquid was dried to constant weight in vacuum over phosphorus pentoxide (2 hr) and then analyzed. The yield was 22 g (45%).

d_4^{20} 1.176, $n^{20}D$ 1.448, MR_D 105.6; calculated 106.3.
Found %: P 13.68. $C_{16}H_{16}O_{11}P_2$. Calculated %: P 13.30.

Tetraethyl octadecaethylene glycol diphosphate. With stirring and cooling, 2.3 g of diethyl chlorophosphate was added dropwise to a mixture of 5 g of octadecaethylene glycol and 1.8 g of triethylamine in 50 ml of absolute ether. The mixture was stirred with gentle heating for a further hour. The precipitate of triethylamine hydrochloride was removed by filtration. The ether was evaporated and the unreacted diethyl chlorophosphate removed in vacuum. The reaction product was extracted from the residue with ether as its solubility in ether was greater than the solubility of the starting octadecaethylene glycol. The product was isolated from the ether solution by cooling the latter to -10°, recrystallized from ether, and dried to constant weight in a vacuum desiccator over phosphorus pentoxide. The yield was 1.7 g (25%).

Found %: P 6.09. $C_{44}H_{92}O_{25}P_2$. Calculated %: P 5.74.

Tetraethyl dotetracontaethylene glycol diphosphate. With stirring and cooling, 0.9 g of diethyl chlorophosphate was added dropwise to a solution of 5 g of the polyethylene glycol containing 42 ethylenoxy groups and 0.96 g of triethylamine in 50 ml of dry ether. The mixture was stirred and heated gently for 1 hr. The precipitate of triethylamine hydrochloride was removed. The reaction product crystallized from the ether solution on prolonged cooling. The product was collected and recrystallized from ether at -20°. The white powder deliquesced to a thick, vaseline-like mass at room temperature in air. It was carefully dried to constant weight in a vacuum desiccator over phosphorus pentoxide. The yield was 1.6 g (30%).

Found %: P. 3.34. $C_{92}H_{185}O_{49}P_2$. Calculated %: P. 2.90.

Mono- and dichloroacetates of polyethylene glycols (Table 3). With stirring and cooling to 0°, to the polyethylene glycol was slowly added monochloroacetyl chloride in a ratio of 1 or 2 moles per mole of polyethylene glycol. The temperature of the mixture rose to 18-20° during the reaction. Stirring was continued for a further 30-40 min at room temperature. The hydrogen chloride was removed in vacuum with slight heating of the mixture. The residue, which consisted of a viscous liquid, was vacuum distilled in the case of low-molecular products. Polyethylene glycol dichloroacetates containing 14 and 18 ethylenoxy groups were treated with ether, isolated from the ether solution as a flocculent precipitate by prolonged cooling to -10 to -15°, and reprecipitated from ether. After prolonged drying in a vacuum desiccator, the reaction products at room temperature consisted of very viscous, yellow, vaseline-like masses which dissolved readily in alcohol, benzene, and dioxane. The lower representatives of this series were insoluble in water, but with an increase in the number of ethylenoxy groups in the molecule (beginning with n = 14), they began to dissolve partly.

Viscosity measurement. The relative viscosity was measured in an Ostwald viscometer with a capillary diameter of 0.6 mm. Dioxane was used as the solvent. It was purified by treatment with dilute hydrochloric acid, standing over potassium hydroxide, and boiling over sodium for 14 hr [3]. The viscosity was measured in a thermostat at 20 ± 0.1°.

SUMMARY

Individual polyethylene glycols with molecular weights from 200 to 8,000 and mono- and diphosphates, and mono- and dichloroacetates of polyethylene glycols were prepared and characterized.

LITERATURE CITED

1. R. Forgyce, H. Lovell, H. Hibert, J. Am. Chem. Soc. 61, 1905 (1939).
2. H. Staudinger. High-Molecular Organic Compounds [Russian translation] ONTI (1933).
3. Yu. K. Yur'ev. Practical Work in Organic Chemistry [in Russian] M., Izd. MGU (1957).

ADDITION OF AROMATIC DERIVATIVES TO VINYLMETHYLDICHLOROSILANE

K. A. Andrianov, A. A. Zhdanov, and V. A. Odinets

Translated from Zhurnal Obshchei Khimii, Vol. 31, No.12,
pp. 4033-4038, December, 1961
Original article submitted November 29, 1960

The addition of aromatic derivatives to vinylchlorosilanes is a convenient method of synthesizing aryl-aliphatic chlorosilanes. The addition of vinyl trichlorosilane to benzene was first described by Wagner and his coworkers [1], who synthesized (β-phenylethyl) trichlorosilane by the direct addition of benzene to vinyltrichlorosilane in the presence of a small amount of aluminum chloride.

$$C_6H_6 + CH_2 = CHSiCl_3 \xrightarrow{AlCl_3} C_6H_5CH_2CH_2SiCl_3$$

Our investigations showed that methylvinyldichlorosilane reacts readily with aromatic hydrocarbons in the presence of aluminum chloride and forms (β-arylethyl)methyldichlorosilanes. As starting materials we used methylvinyldichlorosilane and aromatic derivatives (benzene, toluene, chlorobenzene, and biphenyl). Vinylmethyldichlorosilane was arylated according to the scheme:

$$RH + CH_2{=}CH(CH_3)SiCl_2 \xrightarrow{AlCl_3} RCH_2CH_2(CH_3)SiCl_2$$

$R = C_6H_5,\ CH_3C_6H_4,\ ClC_6H_4.$

$$C_6H_5C_6H_5 + CH_2{=}CH(CH_3)SiCl_2 \xrightarrow{AlCl_3} C_6H_5C_6H_4CH_2CH_2(CH_3)SiCl_2$$

As our investigations showed, these reactions give high yields of (β-arylethyl)methyldichlorosilanes (60-65%). However, considerable amounts of high-boiling products are formed. The addition of vinylmethyldichlorosilane to aromatic hydrocarbons may not be limited to only one molecule of vinylmethyldichlorosilane.

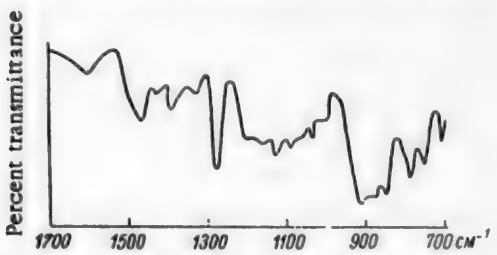


Fig. 1. Infrared spectrum of (phenylethyl)-methylsilanediol.

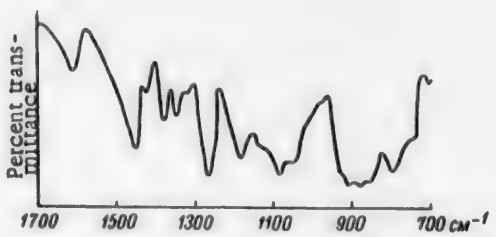
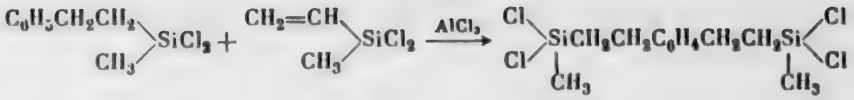


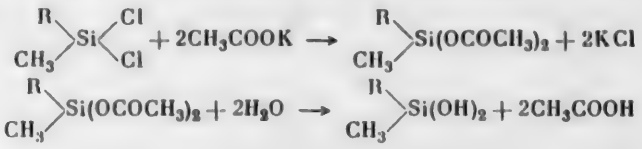
Fig. 2. Infrared spectrum of (tolylethyl)-methylsilanediol.

Experiments showed that treatment of (β-phenylethyl)methyldichlorosilane with vinylmethyldichlorosilane in the presence of aluminum chloride resulted in the addition of a second molecule of vinylmethyldichlorosilane according to the scheme:



It was possible to isolate pure bis(2-dichloromethylsilylethyl)benzene in 35% yield.

For more complete characterization and identification of the arylalkylmethyldichlorosilanes, they were converted into the corresponding acetoxy derivatives and then arylalkylmethylsilanediols according to the scheme:



The infrared spectra of the arylalkylmethylsilanediols synthesized were plotted and are given in Figs. 1-4. In these figures one can see the characteristic absorption bands corresponding to the Si−CH_3 bond (1258 cm^{-1}) and the aromatic ring (1600 cm^{-1}) and also an absorption band at 830-880 cm^{-1}, which can be assigned reliably to a hydroxyl group attached to a silicon atom [2]. In addition, all the compounds investigated showed a strong absorption band in the region of 3250 cm^{-1}, corresponding to valence vibrations of the Si−OH bond. Unfortunately, the infrared spectral data do not make it possible to draw definite conclusions on the position of the substituents; however, from data on the orienting effect of substituents in the aromatic nucleus and an investigation of the infrared spectra of cyclic (phenylethyl)methylsiloxanes it can be concluded that the aromatic ring adds to the vinyl group in the β-position with the substituent in the nucleus in the para-position relative to the organosilicon radical [3]. The properties of the compounds synthesized are given in the table.

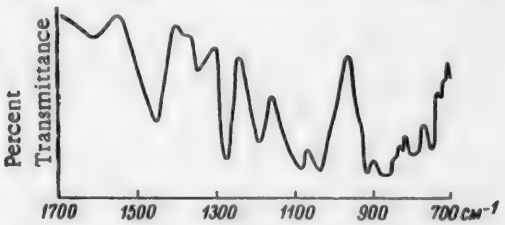


Fig. 3. Infrared spectrum of (chlorophenylethyl)methylsilanediol.

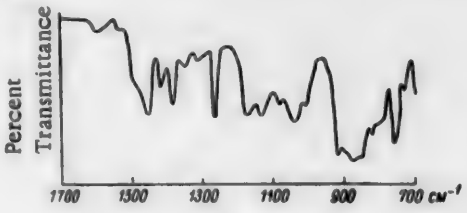


Fig. 4. Infrared spectrum of (biphenylethyl)methylsilanediol.

EXPERIMENTAL

(Phenylethyl)methyldichlorosilane. Into a flask fitted with a thermometer, stirrer, and reflux condenser, were placed 5 g of aluminum chloride, 70.5 g of methylvinyldichlorosilane, and 78 g of freshly distilled benzene. After 3-5 min, the reaction mixture began to boil spontaneously and the contents of the flask darkened. Boiling ceased after 15-20 min and then the reaction mixture was heated at 75-80° for 1.5-2 hr with vigorous stirring. The reaction product was then cooled to 0°, the aluminum chloride removed by filtration, and 2.5 g of triethylamine added to the filtrate. Fifteen to twenty minutes after the addition of the triethylamine, the reaction mixture was again filtered, the solvent (unreacted benzene) removed, and the residue vacuum distilled. We obtained 61 g (55.6%) of the product.

B.p. 90-92° (5 mm), d_4^{20} 1.1270, n_D^{20} 1.5120, MR_D 58.51; Calcu 58.35.
Found %: C 49.07, 49.24; H 5.53, 5.58; Si 12.91, 12.86; Cl 32.11; 32.13. $C_9H_{12}SiCl_2$. Calculated %: C 49.32; H 5.51; Si 12.80; Cl 32.35.

(Tolylethyl)methyldichlorosilane. Into a flask were placed 141 g of methylvinyldichlorosilane, 184 g of toluene, and 10 g of aluminum chloride. The reaction mixture was heated at 90-95° for 2 hr, then the reaction product cooled and filtered, and 5 g of triethylamine added to the filtrate. After 15-20 min, the reaction mixture was filtered again, the toluene removed, and the residue vacuum distilled. We obtained 145 g (62.6%) of the substance.

B.p. 103-105° (2 mm), d_4^{20} 1.1093, n_D^{20} 1.5119, MR_D 63.06; Calcu. 63.16.
Found %: C 51.25, 51.42; H 5.97, 6.06; Si 12.08, 12.40; Cl 30.41, 30.62. $C_{10}H_{14}SiCl_2$. Calculated %: C 51.51; H 6.05; Si 12.03; Cl 30.40.

(Chlorophenylethyl)methyldichlorosilane. Into a flask were placed 141 g of vinylmethyldichlorosilane, 224 g of chlorobenzene, and 10 g of aluminum chloride. The mixture was heated at 90-95° with vigorous stirring for 4 hr, cooled, and filtered to remove aluminum chloride. Then 5 g of triethylamine was added, the mixture filtered again, the excess chlorobenzene removed, and the reaction product vacuum distilled. We obtained 132 g (52.2%) of the substance.

B.p. 124-126° (2 mm), d_4^{20} 1.2306, n_D^{20} 1.5254, MR_D 63.20; Calcu. 63.36.
Found %: C 42.02, 41.98; H 4.42, 4.41, Si 10.70, 10.74; Cl 41.80, 41.98. $C_9H_{11}SiCl_3$. Calculated %: C 42.61; H 4.37; Si 11.06; Cl 41.94.

(Biphenylylethyl)methyldichlorosilane. Into a flask were placed 154.2 g of biphenyl, which had been recrystallized from alcohol, 300 ml of ligroin, and 5 g of aluminum chloride. The mixture was heated to 40° (to obtain a homogeneous solution) and then 70.5 g of methylvinyldichlorosilane added over a period of 10-15 min. The temperature of the mixture thereupon rose by 2-3°. The mixture was heated at 60-70° with vigorous stirring for 3 hr and then cooled and 10 g of triethylamine added. After filtration and removal of the ligroin and then excess biphenyl by distillation, the reaction product was vacuum distilled. We obtained 71.5 g (50%) of the product.

B.p. 180-183° (7 mm), d_4^{20} 1.1602, $n^{20}D$ 1.5770, MR_D 84.33; Calcu. 84.31.
Found %: C 61.23, 61.33; H 5.47, 5.47; Si 9.47, 9.67; Cl 23.60, 23.66. $C_{15}H_{16}SiCl_2$. Calculated %: C 61.01; H 5.46; Si 9.50; C 24.01.

Bis(2-dichloromethylsilylethyl)benzene. Into a flask were placed 146 g of (phenylethyl)methyldichlorosilane, 94 g of methylvinyldichlorosilane, and 6.6 g of aluminum chloride. The mixture was heated at 100-120° with vigorous stirring for 2.5-3 hr. After the addition of 15 g of sodium chloride, the reaction mixture was stirred for a further 20-30 min, cooled, and filtered. The filtrate was vacuum distilled. We obtained 84 g of the substance.

B.p. 176-180° (3 mm), d_4^{20} 1.2102, n_D^{20} 1.5205, MR_D 90.24; Calcu. 90.53.
Found %: C 40.00, 39.86; H 5.04, 5.07; Si 15.45, 15.27; Cl 39.33, 39.47. $C_{12}H_{18}Si_2Cl_4$. Calculated %: C 40.02; H 5.04; Si 15.57; Cl 39.35.

Acetylation of (arylethyl)methyldichlorosilanes. Into a flask fitted with a thermometer, stirrer, and reflux condenser were placed 2.2 mole of the arylethylmethyldichlorosilane, 0.4 mole of anhydrous potassium acetate, and 100 ml of freshly distilled toluene. The mixture was stirred at 100-110° for 8-10 hr, cooled, and filtered (to remove potassium chloride); after removal of the toluene, the acetate group content of the residue was determined. The yield of (arylethyl)methyldiacetoxysilanes was 88-90%. Without further purification, the (arylethyl)methyldiacetoxysilanes obtained were used for the preparation of (arylethyl)methylsilanediols.

(Phenylethyl)methylsilanediol. Into a separatory funnel were placed 45 g of 30% sodium sulfite, 15 ml of ether, 15 ml of concentrated ammonia solution, and a few lumps of ice. Then 15 g of (phenylethyl)methyldiacetoxysilane was added very rapidly with vigorous mixing. The ether layer was washed three times with cold water, dried with sodium sulfate, and filtered into a Petri dish. When the ether had evaporated, there remained in the dish a white crystalline mass, which was dissolved in benzene. The addition of ligroin in small portions to the benzene solution precipitated white crystals. The substance obtained was reprecipitated from a mixture of benzene and a small amount of ether with ligroin. The (phenylethyl)methylsilanediol formed scaly white crystals with m.p. 70°.

Found %: C 59.70, 59.91; H 7.77, 7.93; Si 15.57, 15.35. $C_9H_{14}O_2Si$. Calculated %: C 59.29; H 7.74; Si 15.40.

(Tolylethyl)methylsilanediol was obtained by the above procedure from 16.8 g of (tolylethyl)methyldiacetoxysilane, 45 g of 30% sodium sulfite solution, 15 ml of ammonia, and 30 ml of ether. Recrystallization yielded scaly white crystals with m.p. 70°.

Found %: C 61.84, 61.96; H 8.49, 8.40; Si 14.57, 14.74. $C_{10}H_{16}O_2Si$. Calculated %: C 61.18; H 8.21; Si 14.29.

(Chlorophenylethyl)methylsilanediol. This was obtained analogously from 18 g of (chlorophenylethyl)methyldiacetoxysilane, 45 g of 30% sodium sulfite, 15 ml of ammonia, and 30 ml of ether. Two reprecipitations yielded white scaly crystals with m.p. 89-91°.

Substance	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D		% C		% H		% Si		% Cl	
				Calcu.	Found	Found	Calcu	Found	Calcu	Found	Calcu	Found	Calcu
(Phenylethyl)methyldichlorosilane $C_6H_5CH_2CH_2Si(CH_3)Cl_2$	90—92° (5)	1.1270	1.5120	58.35	58.51	49.07, 49.24	49.32	5.53, 5.58	5.51	12.91, 12.86	12.80	32.11, 32.13	32.35
(Tolylethyl)methyldichlorosilane $CH_3C_6H_4CH_2CH_2Si(CH_3)Cl_2$	103—105 (2)	1.1033	1.5119	63.16	63.06	51.25, 51.42	51.51	5.97, 6.06	6.05	12.08, 12.40	12.03	30.41, 30.62	30.40
(Chlorophenylethyl)methyldichlorosilane $ClC_6H_4CH_2CH_2Si(CH_3)Cl_2$	124—126 (2)	1.2306	1.5254	63.36	63.20	42.01, 41.98	42.61	4.42, 4.41	4.37	10.70, 10.74	11.06	41.80, 41.98	41.94
(Biphenylylethyl)methyldichlorosilane $C_6H_5C_6H_4CH_2CH_2Si(CH_3)Cl_2$	180—183 (7)	1.1602	1.5770	84.31	84.33	61.23, 61.33	61.01	5.47, 5.47	5.46	9.47, 9.67	9.50	23.60, 23.66	24.11
Bis(2-dichloromethylsilylethyl)-benzene $Cl_2Si(CH_3)CH_2CH_2C_6H_4CH_2CH_2Si(CH_3)Cl_2$	176—180 (3)	1.2102	1.5205	90.24	90.53	40.00, 39.86	40.02	5.04, 5.07	5.03	15.45, 15.27	15.57	39.33, 39.47	39.35
(Phenylethyl)methylsilanediol $C_6H_5C_2H_4(CH_3)Si(OH)_2$	M.p. 80—81°	—	—	—	—	59.70, 59.91	59.29	7.77, 7.93	7.74	15.57, 15.35	15.40	18.82,* 18.66*	18.65*
(Tolylethyl)methylsilanediol $CH_3C_6H_4C_2H_4(CH_3)Si(OH)_2$	M.p. 70°	—	—	—	—	61.84, 61.96	61.18	8.49, 8.40	8.21	14.57, 14.74	14.29	17.93,* 17.64*	17.38*
(Chlorophenylethyl)methylsilanediol $ClC_6H_4C_2H_4(CH_3)Si(OH)_2$	M.p. 89—91°	—	—	—	—	49.73, 49.69	49.87	5.93, 5.97	6.04	13.20, 12.75	12.94	15.21, 15.28	15.68
(Biphenylylethyl)methylsilanediol $C_6H_5C_6H_4C_2H_4(CH_3)Si(OH)_2$	M.p. 132—134°	—	—	—	—	71.04, 70.99	70.25	7.18, 7.26	7.02	10.77, 10.97	10.86	—	—

* The % OH is given.

Found %: C 49.73, 49.69; H 5.93, 5.97; Si 12.75, 13.20; Cl 15.91, 16.10. $C_9H_{13}O_2SiCl$. Calculated %: C 49.87; H 6.04; Si 12.94; Cl 16.36.

(Biphenylylethyl)methylsilanediol. This was obtained analogously from 20.5 g of (biphenylylethyl)methyldiacetoxysilane, 45 g of 30% sodium sulfite, 15 ml of ammonia, and 30 ml of ether. The white crystalline substance had m.p. 132-134°.

Found %: C 71.04, 70.99; H 7.18, 7.26; Si 10.77, 10.97. $C_{18}H_{18}O_2Si$. Calculated %: C 70.25; H 7.02; Si 10.86.

SUMMARY

1. The addition of aromatic hydrocarbons to vinylmethyldichlorosilane was studied and it was shown that this reaction forms (β-arylethyl)methyldichlorosilanes and derivatives of bis(2-dichloromethylsilylethyl)benzene.

2. (Phenylethyl)methyldichlorosilane, (tolylethyl)-methyldichlorosilane, (chlorophenylethyl)methyldichlorosilane, (biphenylylethyl)methyldichlorosilane, and bis-(2-dichloromethylsilylethyl)benzene were synthesized and their properties studied.

3. It was shown that the reaction of (arylethyl)methyldichlorosilanes with potassium acetate forms (arylethyl)-methyldiacetoxysilanes, which, on subsequent hydrolysis with water under mild conditions, form (arylethyl)methylsilanediols. (Phenylethyl)methylsilanediol, (tolylethyl)-methylsilanediol, (chlorophenylethyl)methylsilanediol, and (biphenylylethyl)methylsilanediol were synthesized.

LITERATURE CITED

1. G. H. Wagner, D. L. Bailey, A. H. Pines, M. L. Dunham Ind. Eng. Ch., No 2, 368 (1953).
2. R. E. Richard, H. W. Thompson, J. Chem. Soc. 1949, 124.
3. K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, Izv. AN SSSR 1961,1615.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

HYDROLYSIS OF CYCLIC POLYMETHYLSILAZANES

K. A. Andrianov and G. Ya. Rumba

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4038-4042, December, 1961
Original article submitted January 2, 1961

The Si–N bond undergoes hydrolysis and alcoholysis extremely readily. This property is used for analytical purposes. Thus, for the determination of nitrogen in the nitrogen-containing organosilicon compounds $n\text{-}C_3H_7Si(NHR)_3$ [1], $(CH_3)_3SiNHR$ [2], $(n\text{-}C_3H_7)_3SiNR_2$ [3], $[(CH_3)_3Si]_2NH$ [4], $[(CH_3)_2SiNH]_3$, $[(CH_3)_2SiNH]_4$ [5,6] they are boiled with HCl in water, aqueous alcohol, or aqueous acetone, when the silazanes decompose to form siloxanes and ammonium or the corresponding amine salts. There have been no systematic investigations of the hydrolysis of compounds containing the Si–N bond in relation to the structure of the molecule and the hydrolysis medium. It has been reported that the hydrolysis resistance of aminosilanols increases with an increase in the size of the radical at the nitrogen. It has also been reported that acids hydrolyze the Si–N bond more rapidly than water and alkalis [8-10]. Alcohols break this bond more readily than water. The alcoholysis rate falls with an increase in the size of the hydrocarbon radical in the alcohol molecule [11]; this reaction is used for synthetic purposes [12, 13].

The hydrolysis resistance of compounds with Si–N bonds containing alkoxyl [11], ester [14-17], and sulfone groups [18] is considerably reduced. The Si–N bond in alkylsilylhydrazines is also hydrolyzed readily [19, 20], but a phenyl group at the silicon atom increases the hydrolysis resistance [10, 21, 22]. Some authors mistakenly regard hexamethylcyclotrisilazane and octamethylcyclotetrasilazane as substances that are hydrolyzed very readily and suggested their use in the waterproofing of paper, on the surface of which they should be hydrolyzed by absorbed water and form polymers [23].

Cyclic polydimethylsilazanes are of considerable interest for the preparation of polymers with Si–N–Si bonds and also for their conversion into polydimethylsiloxanes. In the present work we investigated the hydrolysis of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane in various media.

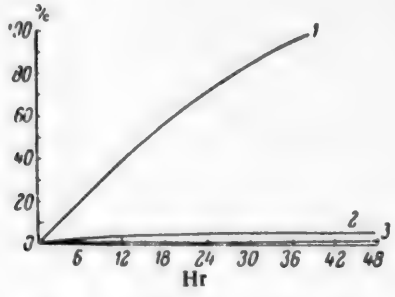


Fig. 1. Hydrolysis of octamethylcyclotetrasilazane in toluene. 1) Hydrolysis by water; 2) by 1.8 N potassium hydroxide solution; 3) by 0.1 N potassium hydroxide solution.

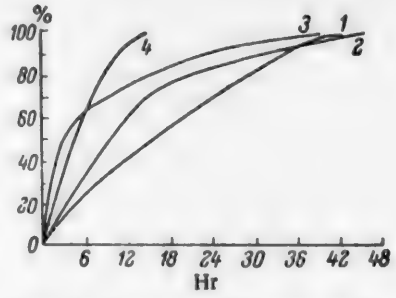


Fig. 2. Hydrolysis of octamethylcyclotetrasilazane in toluene. 1) By 0.5 N hydrochloric acid; 2) by 0.1 N sulfuric acid; 3) by 0.5 N sulfuric acid; 4) by 0.3 N ammonium sulfate solution.

The hydrolysis was carried out by boiling with water in the presence of acids, alkalis, and ammonium salts in heterogeneous (toluene and diethyl ether) and homogeneous media (acetone, methanol, ethanol, and isobutanol). The experimental data are given in Figs. 1-8. In the investigation of the hydrolysis resistance of octamethylcyclotetrasilazane in the heterogeneous medium toluene–water, it was found that the hydrolysis proceeded slowly (Fig. 1). Only boiling the mixture for 40 hr led to complete hydrolysis of the octamethylcyclotetrasilazane. The addition

of alkali (0.5 and 10% of potassium hydroxide) strongly retarded the hydrolysis of octamethylcyclotetrasilazane. Only 1.4% of the octamethylcyclotetrasilazane was hydrolyzed by boiling in the presence of 0.5% of KOH for 48 hr. The hydroxyl ion had the same retarding effect on the hydrolysis of octamethylcyclotetrasilazane in acetone (Fig. 4) and diethyl ether (Fig. 5), where the curves of hydrolysis in the presence of potassium hydroxide differ markedly from the others.

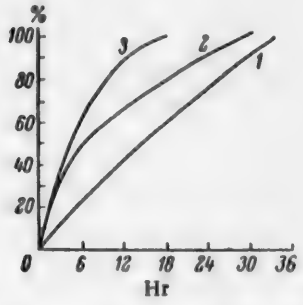


Fig. 3. Hydrolysis of hexamethylcyclotrisilazane in toluene. 1) By water; 2) by 0.5 N sulfuric acid; 3) by 0.3 N ammonium sulfate solution.

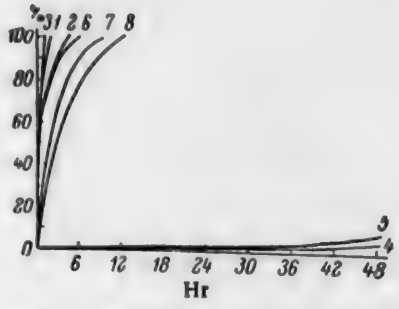
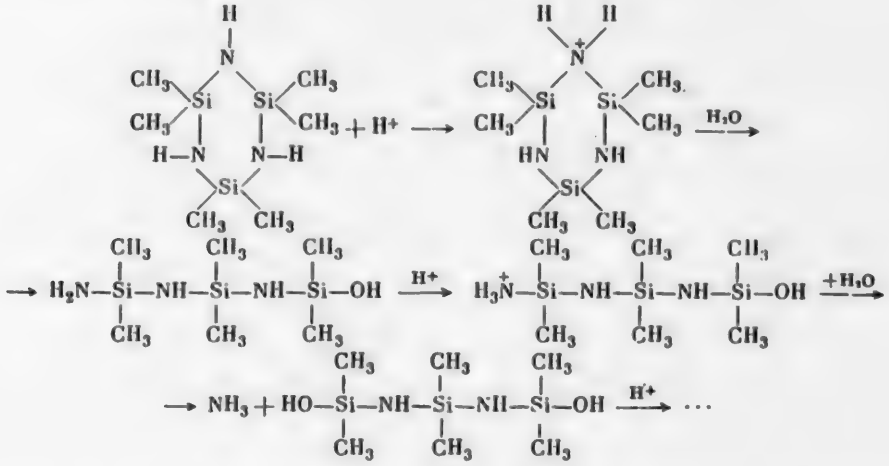


Fig. 4. Hydrolysis in acetone. Hydrolysis of octamethylcyclotetrasilazane: 1) by 10% water; 2) by 50% water; 3) by 0.01 N sulfuric acid (10% water); 4) by 0.2 N potassium hydroxide solution (10% water); 5) by 0.1 N potassium hydroxide solution (10% water). Hydrolysis of hexamethylcyclotrisilazane: 6) by wet acetone; 7) by 0.1 N potassium hydroxide solution (10% water); 8) by 1 N potassium hydroxide solution (10% water).

The introduction of substances capable of forming a hydrogen ion in aqueous media had a completely opposite effect. In this case, the hydrolysis of both octamethylcyclotetrasilazane and hexamethylcyclotrisilazane in all media proceeded much more rapidly than in water (Figs. 2,3,4, and 5). From this it can be concluded that the hydrolyzing agent in water is the hydrogen ion (formed in small amounts by its dissociation).



In alkaline solutions, the effect of the hydrogen ion is suppressed by the hydroxyl ions and therefore the hydrolysis rate is sharply reduced. This is not contradicted by the fact that the hydrolysis in the presence of ammonium sulfate proceeds much more rapidly than in water (Figs. 2 and 3) as the hydrolysis of this salt leads to the formation of hydrogen ions. The hydrolysis in a homogeneous aqueous acetone medium proceeded much more rapidly than in toluene. The comparatively low rate of hydrolysis in diethyl ether is explained by the low boiling point.

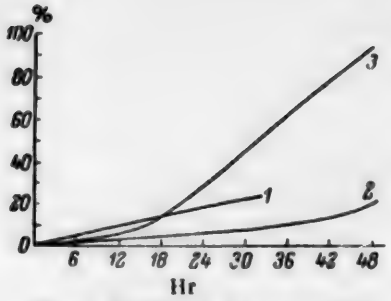


Fig. 5. Hydrolysis of octamethylcyclotetrasilazane in diethyl ether. 1) By 10% water; 2) by 0.01 N potassium hydroxide solution (10% water); 3) by 0.01 N sulfuric acid (10% water).

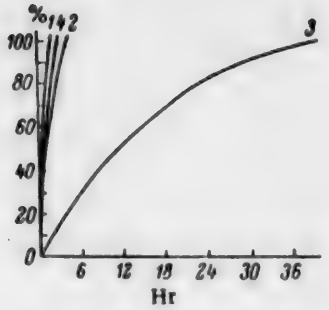


Fig. 6. Alcoholysis in ethanol. Alcoholysis of octamethylcyclotetrasilazane: 1) in absolute alcohol; 2) in 96% alcohol; 3) by a 0.1 N solution of potassium hydroxide in absolute alcohol. Alcoholysis of hexamethylcyclotrisilazane: 4) in 96% alcohol.

The processes occurring in alcohols differ from those in other solvents. As Fig. 6 shows, the liberation of ammonia occurred most rapidly in anhydrous alcohol, i.e., in a practically anhydrous medium in which the probability of hydrolysis is low. In this case there occurs alcoholysis, whose rate (Fig. 6, curve 1) falls in the presence of water.

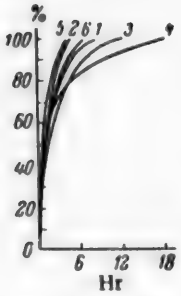


Fig. 7. Alcoholysis in methanol. Alcoholysis of octamethyl cyclotetrasilazane: 1) without additives; 2) by 50% water; 3) by 0.01 N potassium hydroxide solution (10% water), 4) by 0.1 N potassium hydroxide solution. Alcoholysis of hexamethylcyclotrisilazane: 5) without additives; 6) by 0.1 N potassium hydroxide solution.

Data obtained in experiments in methanol and isobutanol also indicate the high tendency of octamethylcyclotetrasilazane and hexamethylcyclotrisilazane for alcoholysis. The rates of the processes in methanol, ethanol, and isobutanol are similar and the alcoholysis rate falls with an increase in the size of the hydrocarbon radical. The introduction of alkali (KOH) retards alcoholysis.

The experimental data on the hydrolysis and alcoholysis of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane show that hexamethylcyclotrisilazane is hydrolyzed more rapidly than octamethylcyclotetrasilazane. A similar phenomenon was observed with cyclic siloxanes: a six-membered ring is opened more readily than an eight-membered ring [24].

Attempts to hydrolyze hexamethylcyclotrisilazane and octamethylcyclotetrasilazane with moist air did not give positive results as despite their comparatively high boiling points (188° for hexamethylcyclotrisilazane and 255° for octamethylcyclotetrasilazane), these substances readily volatilized with air. This shows that the use of these compounds for waterproofing is ineffective as only a temporary effect may be achieved (especially in the case of constructional materials where the conditions are unfavorable for the hydrolysis of these compounds).

EXPERIMENTAL

The apparatus shown in Fig. 9 was used for the hydrolysis. Into the flask A were placed 3.65 g of hexamethylcyclotrisilazane or octamethylcyclotetrasilazane, 45 ml of solvent, and 5 ml of water. The ammonia liberated was trapped in water in flask B and titrated with 0.5 N sulfuric acid in the presence of Methyl orange. The wide section C in the connecting tube prevented water from being sucked from flask B into flask A by the rapid solution of the ammonia liberated in the water. The contents of flask A were boiled continuously until the liberation of ammonia was complete and heating was continued for 48 hr. The ammonia dissolved in flask B was titrated every half hour and the amount of acid required for the titration recorded (D). At the end of the experiment, flask A and the connecting system were flushed so that the ammonia in them dissolved in the water in flask B. The data obtained are given in Figs. 1-8.

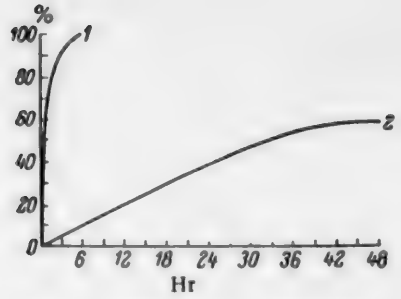


Fig. 8. Alcoholysis of octamethylcyclotetrasilazane in isobutanol. 1) Without additives; 2) by 0.1 N potassium hydroxide solution.

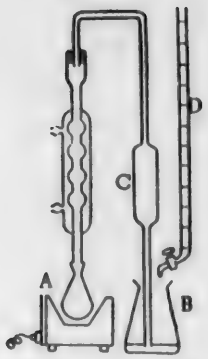


Fig. 9. Hydrolysis apparatus. Explanation in text.

SUMMARY

1. It was established that hexamethylcyclotrisilazane and octamethylcyclotetrasilazane have a relatively high resistance to hydrolysis in neutral and especially alkaline media.

2. Hydrogen ions catalyze the hydrolysis of hexamethylcyclotrisilazane and octamethylcyclotetrasilizane, while hydroxyl ions sharply retard it.

3. Hexamethylcyclotrisilazane (six-membered ring) is hydrolyzed more rapidly than octamethylcyclotetrasilazane (eight-membered ring).

4. Hexamethylcyclotrisilazane and octamethylcyclotetrasilazane react readily with alcohols; alcoholysis is retarded in the presence of alkalis.

LITERATURE CITED

1. L. Tansjö, Acta Chem. Scand. 11, 1613 (1957).
2. O. Mjörne, Svensk. Kemisk. Tidskrift. 62, No 4, 120 (1950).
3. E. Larsson, R. Mårin, Acta Chem. Scand. 5, 1173 (1951).
4. R. O. Sauer, J. Am. Chem. Soc. 66, 1707 (1944).
5. E. Larsson, B. Smith, Acta Chem. Scand. 3, 487 (1949).
6. S. D. Brewer, Ch. P. Haber, J. Am. Chem. Soc. 70, 3888 (1948).
7. K. A. Andrianov, S. A. Golubtsov, E. A. Semenova, Izv. AN SSSR, OKhN 1958, 47.
8. R. O. Sauer, R. H. Hasek, J. Am. Chem. Soc. 68, 241 (1946).
9. S. H. Langer, S. Connell, J. Wender, J. Org. Ch. 23, 50 (1958).
10. E. Larsson, L. Bjellrup, J. Am. Chem. Soc. 75, 995 (1953).
11. C. S. Miner, L. A. Bryan, R. P. Holysz, G. W. Pedlow, Ind. Eng. Ch. 39, 1368 (1947).
12. L. H. Sommer, F. C. Whitmore, A. D. Philip, Giorgio, J. Am. Chem. Soc. 71, 3254 (1949).
13. A. P. Kreshkov, L. V. Myshlyaeva, L. M. Khananashvili, ZhOKh 28, 2112 (1958).
14. L. Birkofer, A. Ritter, Lieb. Ann. 612, 22 (1958).
15. L. Birkofer, A. Ritter, Ang. Chem. 68, 461 (1956).
16. K. Rühlman, J. pr. Ch. 9, 86 (1959).
17. R. Schwarz, Fr. Weigel, Z. anorg. allg. Chem. 268, 291 (1952).
18. M. Becke-Godning, G. Wunsch, Lieb. Ann. 618, 43 (1958).
19. U. Wannagat, W. Liehr, Z. anorg. allg. Chem. 299, 341 (1959).
20. U. Wannagat, W. Liehr, Z. anorg. allg. Chem. 297, 129 (1958).
21. M. V. George, D. Wittenberg, H. Gilman, J. Am. Chem. Soc. 81, 361 (1959).
22. D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles, H. Gilman, J. Am. Chem. Soc. 80, 4532 (1958).
23. N. T. Belen'kaya, M. G. Voronkov, B. N. Dolgov, ZhPKh 28, 886 (1955).
24. N. N. Sokolov, ZhOKh 28, 3328 (1958).

PREPARATION OF HEMI-CHLORONITROSO HYDROCARBONS

A. E. Kretov, E. A. Abrazhanova, and S. I. Zlotchenko

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4043-4044, December 1961
Original article submitted October 31, 1960

Hemi-chloronitroso hydrocarbons are nitroso compounds which exist in a monomeric form. Several methods of preparing them are described in the literature.

The first compounds of this type were prepared by Piloty and Steinbock [1] by the action of chlorine or bromine on hydrochloric acid solutions of aldehyde and ketone oximes. As Paoliny [2] showed later, this reaction is not general and depends on the radicals attached to the carbonyl group. Later, Reinbold and Dewald [3-5] obtained α-halonitroso hydrocarbons by the action of nitrosyl chloride on oximes. The same result was achieved by a number of authors [6-9] by the action of nitrosyl chloride on hydrocarbons. In studying the chlorination products of 2-nitroindandione monooxime, Vanag and Vitol' [10] obtained 1-chloro-1-nitroso-2-nitroindanone. By the action of a mixture of chlorine and nitric oxide on cyclohexane under irradiation by ultraviolet light, Miller and Metzger [11] obtained the corresponding α-chloronitrosohydrocarbon. In this case the reaction proceeds with the formation of free radicals. However, the formation of hemi-chloronitrosocyclohexane was accompanied by a series of side reactions and the fraction isolated by Miller and Metzger had quite a wide boiling range [40-70° (18 mm)]; the yield of the individual substance was not given.

We obtained hemi-chloronitroso hydrocarbons by the action of N-dichloroarenesulfonamides on aliphatic and aromatic aldehyde and ketone oximes.

The reaction of -diketone oximes with chloramine was studied by Forster [12] and Meinwald [13]. Forster showed that the reaction of an -oximino ketone with chloramine gives diazo ketones in insignificant yields.

The mechanism of Forster's reaction was studied recently by Meinwald, Gassman, and Miller. They increased the yields of diazo ketones somewhat by replacing chloramine by a hydroxylamino-o-sulfonic acid. It was found that the reaction of aldehyde and ketone oximes with N-dichloroarenesulfonamides proceeds very vigorously (with heat evolution) and may be represented by the scheme:

$$2>C{=}NOH + ArSO_2NCl_2 \longrightarrow 2>C\begin{matrix}NO\\Cl\end{matrix} + ArSO_2NH_2$$

The reaction was carried out with the oximes of acetaldehyde, methyl ethyl ketone, cyclohexanone, benzaldehyde, acetophenone, and salicylaldehyde. All the reaction products, apart from that from benzaldehyde, gave a positive Liebermann reaction for a nitroso group. As reported in the literature [15, 14], α-nitrosobenzyl chloride isomerizes readily to benzhydroxamyl chloride according to the scheme:

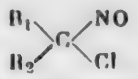
$$C_6H_5{-}C\begin{matrix}H\\NO\\Cl\end{matrix} \longrightarrow C_6H_5C\begin{matrix}Cl\\\\NOH\end{matrix}$$

This conversion occurs at the moment of formation of the α-nitrosobenzyl chloride and corresponds to the change in color from dark blue to yellow. The nitroso group was not detected in the product obtained, but boiling with alkali, subsequent addition of ferric chloride, and acidification gave the red color characteristic of hydroxamic acid derivatives. The chloronitroso derivative obtained from salicylic acid existed as a dimer, as is clear from the value obtained for the molecular weight. No rearrangement into a hydroxamic acid derivative occurred and the Liebermann reaction confirmed the presence of a nitroso group.

EXPERIMENTAL

Reaction of N-dichlorobenzenesulfonamide with aldoximes and ketoximes. A solution of 0.05 mole of dichloramine B in benzene or another organic solvent was added dropwise to 0.05 mole of the oxime in a three-necked flask with a reflux condenser, dropping funnel, and thermometer. The solvent chosen was such that its boiling point differed appreciably from that of the chloronitroso compound formed. The temperature of the reaction mixture was not allowed to exceed 25-30° (to avoid decomposition of the chloronitroso compound). After the reaction mixture had been cooled, the precipitate of benzenesulfonamide was removed by filtration and the filtrate vacuum distilled with the fraction boiling over the range given below collected. In the case of salicylaldehyde oxime, the solid residue after removal of the solvent in vacuum was recrystallized from carbon tetrachloride.

Properties of α-Chloronitroso Hydrocarbons



R_1	R_2	Boiling Point (Pressure in mm)		Melting Point		% N		Yield (%)	M
		accord. to Liter. data	Found	accord. to Liter. data	Found	Calcu.	Found		
CH_3	H	60°	68—72°	—	—	7.6	7.5	21	—
CH_3	C_6H_5	—	81—82	—	—	11.5	10.8	26.6	—
(C_5H_{10})	C_6H_{10}	50 (18)	40—50 (16)	—	—	9.4	8.2	51	—
C_6H_5	H	—	—	48°	42—45°	9.1	8.7	82	—
C_6H_5	CH_3	—	214—220	—	—	8.3	7.5	35	—
OC_6H_4	H	—	—	—	106	8.2	8.3	29	336

SUMMARY

A new method is proposed for the preparation of hemi-chloronitroso hydrocarbons by treatment of aldoximes and ketoximes with N-dichloroarenesulfonamides.

LITERATURE CITED

1. O. Piloty, M. Steinbock, Ber. 35,3101 (1902).
2. V. Paoliny, Zbl. 1931, II, 2596.
3. H. Reinbold, M. Dewald, Lieb. Ann. 451, 274 (1927).
4. H. Reinbold, M. Dewald, Lieb. Ann. 451, 161 (1927).
5. E. Reinbold, M. Dewald, Lieb. Ann. 455, 300 (1927).
6. E. Lynn, J. Am. Chem. Soc. 41, 368 (1919).
7. E. Lynn, O. Milton, J. Am. Chem. Soc. 44, 645 (1922).
8. S. Michel, S. Carson, J. Chem. Soc. 1936, 1005.
9. M. Naylor, A. Anderson, J. Org. Ch. 18,115 (1953).
10. G. Vanag, V. Vitol', DAN SSSR 89, 857 (1913).
11. E. Miller, H. Metzger, Ber. 87, 1282 (1954).
12. M. O. Forster, J. Chem. Soc. 107, 260 (1915).
13. I. Meinwald, P. Gassman, E. Miller, J. Am. Chem. Soc. 81, 4751 (1959).
14. A. Werner, H. Buss, Ber. 27, 2196 (1894).
15. O. Piloty, M. Steinbock, Ber. 35, 3112 (1902).

SYNTHESIS AND INVESTIGATION OF AMINODESOXY SUGARS

II. N-ARYL DERIVATIVES OF 6-AMINO-6-DESOXYDIACETONE-D-GALACTOSE

V. I. Veksler

F. Engels Leningrad Institute of Soviet Commerce

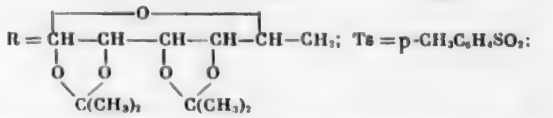
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4045-4051, December, 1961
Original article submitted January 6, 1961

Few arylaminodesoxy sugars are known apart from derivatives of 1-amino-1-desozy ketoses, which can be obtained by the Amadori transformation [1]; moreover, only isolated substances have been described (methyl 4,6- benzylidene-2-anilino-2-desoxy-α-D-mannopyranoside [2a], phenylaminoxylitan [2b], N-2,4-dinitrophenylglucosamine [2c], and N-phenyl- and N-p-tolylglucosamines [2d]).

The purpose of the present work was the synthesis of compounds of this class and, in particular, N-aryl derivatives of 6-amino-6-desoxy-D-galactose. At the same time, we obtained some data of a general nature on the mechanism of the formation of aminodesoxy sugars from sulfonic esters.

These compounds were synthesized by heating (~100°) aromatic amines with 6-tosyldiacetone-D-galactose (subsequently denoted by Ts-DAG) without a solvent or in n-butanol, dioxane, pyridine, or toluene; in the later case, however, the reaction proceeded slowly. The reaction proceeded according to the over-all equation:

$$R{-}OTs + 2ArNH_2 \longrightarrow \underset{(I)}{R{-}NH{-}Ar} + \underset{(II)}{ArNH_2 \cdot TsOH} \qquad (1)$$



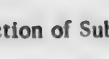
$R =$ (diacetone-D-galactose residue); $Ts = p\text{-}CH_3C_6H_4SO_2$;

$Ar = C_6H_5$ (a), p-$CH_3C_6H_4$ (b), o-$CH_3C_6H_4$ (c), o-$CH_3OC_6H_4$ (d), p-$CH_3OC_6H_4$ (e).

Together with the arylaminodesoxy sugar (I), the reaction also yielded the p-toluenesulfonate of the starting amine (II), which sometimes precipitated. Judging by the amount of the salt (II) formed, the reaction may proceed practically quantitatively (~90%), but the amino sugar was isolated in small amounts. The amino sugars could be isolated by solution in dilute acid and precipitation from this solution with alkali or, better, dilute ammonia solution. When we used excess of an aromatic amine which could be removed by steam distillation, it was removed by this method, but this led to appreciable tar formation by the amino sugar. By the method described we prepared 6-phenylamino-(Ia), 6-p-tolylamino- (Ib), 6-o-tolylamino- (Ic), 6-o-anisylamino- (Id), and 6-p-anisylamino-6-desoxy-1,2:3,4-diisopropylidene-D-galactose (Ie). Apart from (Ic) they all crystallized readily and were readily soluble in most organic solvents and insoluble in water; they formed crystalline N-benzoyl derivatives and, in individual cases, salts with p-toluenesulfonic, oxalic, and hydrochloric acids which were convenient for isolation.

It was found that Ts-DAG reacts with different amines at appreciably different rates. We carried out an experiment with 14 different substituted anilines and α- and β-naphthylamines simultaneously under completely identical conditions as regards temperature and the molecular concentrations of reagents. The reaction rate was determined analytically from the amount of p-toluene-sulfonic acid formed as the salt (II). The results are given in Table 1, which also gives the basicity constants of the amines.

As the data in Table 1 show, the rates of the reactions of amines with Ts-DAG depend directly on the basicity of the amines: the stronger the amine as a base, the faster is the reaction. The reaction with p-anisidine is fastest; nitroanilines react very slowly. The para- and meta-monosubstituted anilines investigated lie in a series with respect to the reaction rate which corresponds completely with the series of the Hammett constants σ [5]:

TABLE 1. Rates of Reaction of Substituted Anilines R-  -NH_2 and Naphthylamines with 6-Tosyldiacetone-D-galactose in Butanol (100°, 8.5 hr, $2.3 \cdot 10^{-4}$ mole of Ts-DAG, $9.26 \cdot 10^{-4}$ mole of amine; volume 2 ml)

Amine (nature of R)	Amino sug. yield (%)	Basicity constant of amine K_a[3]	Amine (nature of R)	Amino sug. yield (%)	Basicity constant of amine K_a[3]
p-CH_3O	54	$5.15 \cdot 10^{-6}$	o-CH_3	14.5	$4.08 \cdot 10^{-5}$
p-CH_3	36.7	$8.51 \cdot 10^{-6}$	α-Naphthylamine	12.4	$1.21 \cdot 10^{-4}$
m-CH_3	26.7	$2.04 \cdot 10^{-5}$	m-NO_2	5.4	—
H	24.1	$2.63 \cdot 10^{-5}$	p-SO_2NH_2	4.4*	—
o-CH_3O	24.1	$3.24 \cdot 10^{-5}$	p-NO_2	3.5	$1.3 \cdot 10^{-2}$ [4]
p-Cl	19.5	$8.51 \cdot 10^{-5}$	o-Cl	3.4	$1.6 \cdot 10^{-3}$ [4]
β-Naphthylamine	18.9	$7.76 \cdot 10^{-5}$	2,4-$(NO_2)_2$	2.2*	—
p-Br	14.8	$1.3 \cdot 10^{-4}$ [4]	2,6-$(Cl)_2$	0	—

*Sulfanilamide and 2,4-dinitroaniline precipitated under the reaction conditions.

p-CH_3O > CH_3 > H > Cl > Br > NO_2; m-CH_3 > H > NO_2.
o-Chloroaniline reacts very slowly and there is hardly any reaction with 2,6-dichloroaniline.

Using the above analytical method, we studied the kinetic order of the reaction investigated for the case of Ts-DAG and p-toluidine in n-butanol at 100° with various initial concentrations of the starting materials. The results of the measurements are given in Figs. 1 and 2, where the fraction of the starting material (Ts-DAG) reacting as a percentage of the original amount is plotted along the ordinate axis. These figures show that the time required for a given fraction of the starting material to react depends on the initial concentration. Since, as is shown by Fig. 1, this time is inversely proportional to the concentrations of the starting materials, the reaction is of the second order [6]. The reaction rate constants calculated from the equation for a bimolecular reaction also remained steady (Table 2).

According to literature data [7, 8], the replacement of an aryl (alkyl)-sulfonyl group in sugar derivatives by an NH_2 or NH_2-NH group, which is used widely for the synthesis of aminodesoxy sugars, proceeds with inversion of the configuration at the C atom to which the aryl (alkyl) sulfonyl group is attached. As this was established for cases where the other OH groups in the molecule were blocked and thus the intermediate formation of anhydro rings or the participation of neighboring groups was completely excluded, the inversion of the configuration led to the hypothesis that the reaction proceeds by an S_N2 mechanism [7]. However, a change in configuration may also occur with an S_N1 mechanism[9].

TABLE 2. Values Found for $k_2^{100°} \cdot 10^3$

Solutions	Solution concentrations (mole/liter)		Sample volume (ml)	Values of $k_2^{100°} \cdot 10^3$ (mole^{-1}/liter/min^{-1}) at the following intermediate times (min)								
	Ts-DAG	p-toluidine		120	180	240	300	360	450	600	550	Mean Value
A	0.138	0.552	2	2.0	—	2.1	—	2.5	2.7	2.8	2.6	2.5
B	0.069	0.226	4	1.8	—	2.0	—	2.2	2.6	2.9	3.0	2.4
C	0.1158	0.463	2	—	2.3	2.4	2.6	2.6	2.2*	—	—	2.5
D	0.0579	0.927		2.5	2.6	2.8	2.8	2.6	2.5*	—	—	2.6

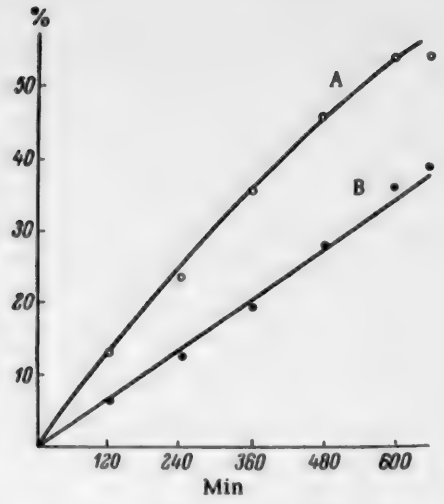


Fig. 1. Rate of reaction of Ts-DAG with p-toluidine at 100° in butanol with an initial concentration ratio of 2 : 1. A) Ts-DAG 0.138 and p-toluidine 0.552; B) DAG 0.069 and p-toluidine 0.226 (in mole/liter).

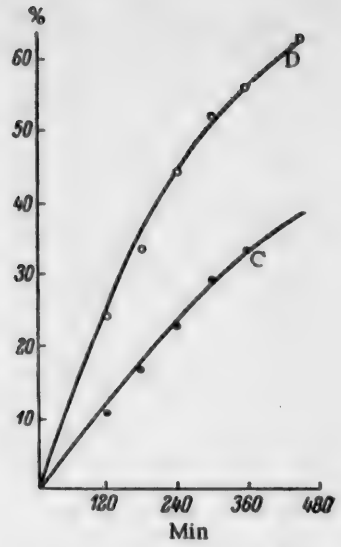


Fig. 2. Rate of reaction of Ts-DAG with p-toluidine at 100° in butanol with various initial concentrations. C) Ts-DAG 0.1158 and p-toluidine 0.463; D) Ts-DAG 0.0579 and p-toluidine 0.927 (mole/liter).

Since, as was shown above, the reaction proceeds according to a kinetic equation of the 2nd order and the reaction rate is substantially affected by the nucleophilicity of the reagent, it can be concluded that the replacement of an aryl (alkyl) sulfonyl group by an amino group in sugars proceeds by an S_N2 mechanism.

EXPERIMENTAL

Synthesis of Arylaminodesoxy Sugars

The starting amines and solvents of "chemically pure" and "analytical" grades were purified by distillation or recrystallization by the usual methods. Ts-DAG was obtained in the usual way [10] and had m.p. 91-92° (from alcohol).

6-p-Tolylamino-6-desoxy-1,2:3,4-diisopropylidene-D-galactose (Ib). a) A mixture of 1.81 g of p-toluidine and 5.2 g of Ts-DAG (150% of the theoretical amount) was heated on a boiling water bath for 11.5 hr. Crystals of the salt began to precipitate 30-40 min after the beginning of heating. To the compact solid mass formed was added ether and the suspension of p-toluidine p-toluene-sulfonate (IIb) collected; it weighed 1.65 g (70.5%), had m.p. 190° (not corr.) (according to literature data [11]: m.p. 196-197 and 199-200°), and was readily soluble in water. The ether solution was shaken repeatedly (5-6 times) with 2 N H_2SO_4 (~20-25-ml portions) until the amine had been extracted completely (no precipitate or turbidity when the sulfuric acid extract was poured into alkali). The sulfuric acid extract was slowly added to excess dilute (~5-10%) ammonia. The next morning, the precipitate of the amino sugar (Ib) was collected, washed on the filter, and dried. It weighed 1.6 g (78%, calculated on the p-toluidine used).

A solution of NaOH or sodium carbonate could be used for reprecipitation instead of ammonia, but in this case the precipitate of the amino sugar was more tarry and did not dissolve completely in ether and the alkaline solution acquired a sharp odor on standing.

For purification, the amino sugar was dissolved in heptane and the hot solution passed slowly through a layer of Al_2O_3, which removed colored impurities. As the heptane solution stood, (Ib) crystallized. For final purification, it was again recrystallized from heptane or aqueous alcohol. The large lustrous and colorless platelets had m.p. 85-85.5°, $[\alpha]_D^{22}$ – 80.3° (CH_3OH, c 7.41).

Found %: C 65.69, 65.93; H 7.91, 7.78. $C_{19}H_{27}O_5N$. Calculated %: C 65.30; H 7.79.

b) A mixture of 1.05 g of p-toluidine and 2 g of Ts-DAG in 3 ml of n-butanol, dioxane, or pyridine was heated at 100° for 14 hr. The salt did not precipitate from pyridine. Reprecipitation from 2 N H_2SO_4 with dilute NH_4OH gave yields of the crude sugar of 49, 37, and 42%, respectively (% of theoretical). There was least tar formation in dioxane.

The substance was soluble in the normal organic solvents, dilute mineral acids, and concentrated (~70%) acetic acid and dissolved very slowly in dilute acetic and oxalic acids.

The amino sugar formed salts with anhydrous oxalic acid in ether. Treatment with a large excess of acid precipitated a white powder with m.p. 77-79°, which corresponded in composition to the formula A · 4$(COOH)_2$ (where A is the amino sugar).

Found %: N 1.92, 1.97. Equiv. 86.4, 88.5. $C_{19}H_{27}O_5N \cdot 4\ (COOH)_2$. Calculated %: N 1.97. Equiv. 88.6.

The use of a small amount of oxalic acid (~2 moles per mole of amino sugar) gave a precipitate with m.p. 160-162° (with decomp.), which corresponded approximately to the formula A · $(COOH)_2$.

Found: Equiv. 232, 232. $C_{19}H_{27}O_5N \cdot (COOH)_2$. Calculated: Equiv. 220.

In individual experiments, the oxalate precipitate formed only after prolonged standing, cooling, rubbing with a rod, etc.

6-Phenylamino-6-desoxy-1,2:3,4-diisopropylidene-D-galactose (Ia). A mixture of 5.75 g of Ts-DAG and 10 ml of aniline (~3.5 fold excess) was heated at 100° for 9.75 hr. The addition of ether precipitated 3.2 g (87%, calculated on the Ts-DAG) of aniline p-toluenesulfonate (IIa) with m.p. 228-230° (m.p. 223 and 235-236° [11]). Aniline was identified in an aqueous solution of the salt. The aniline was distilled from the ether solution with steam. A solid black resin remained in the distillation flask and this was dissolved inether and the solution filtered and dried with Na_2SO_4. From part of the solution we isolated (Ia) by reprecipitation and purification as described above. From heptane we obtained a finely crystalline, colorless powder of (Ia) with m.p. 77-78° $[\alpha]_D^{24}$ –99.5° (butanone-2, c 2.26).

Found %: N 4.60, 4.62. $C_{18}H_{25}O_5N$. Calculated %: N 4.18.

Salts were prepared from part of the ether solution of the reaction products after distillation of the aniline. A crystalline hydrochloride together with a considerable amount of tar was formed with an ether solution of HCl. The hydrochloride had m.p. 122-125° (with decomp.) and was very readily soluble in water, alcohol, methanol, and ethyl acetate. An attempt to reprecipitate it from ethyl acetate or methanol with ether yielded a viscous mass and the salt formed tar when washed with ethyl acetate or chloroform.

The p-toluenesulfonate of the amino sugar was obtained by the reaction of the components in ether and purified by precipitation from ethyl acetate with ether (in a refrigerator). It had m.p. 147-149° and was readily soluble in water, methanol, and alcohol.

Found %: N 2.85, 2.87. $C_{25}H_{33}O_8NS$. Calculated %: N 2.76.

6-o-Tolylamino-6-desoxy-1,2:3,4-diisopropylidene-D-galactose (Ic). A mixture of 2 g of Ts-DAG and 4 ml of o-toluidine was heated at 100° for 16.5 hr. We obtained 74% of o-toluidine p-toluenesulfonate (IIc) with m.p. 179-181° (m.p. 180° [11]). The excess o-toluidine was removed by steam distillation. The distillation residue was dissolved in ether, the amino sugar extracted with dilute hydrochloric acid (1 : 5), and the hydrochloric acid extract filtered into alkali solution. There precipitated a viscous mass, which collected, dried on the filter, and dissolved in ether, leaving a small amount of ether-insoluble material. The ether was evaporated and the residue dissolved in heptane and passed through a column of Al_2O_3 (the use of animal or wood charcoal for decolorizing the ether solution or alcohol or methanol solutions did not give positive results, as with the other amino sugars in the present work). Evaporation of the heptane gave 0.55 g of an uncrystallizable, slightly colored, viscous substance (Ic). The N-benzoyl derivative was obtained by the action of benzoyl chloride on the amino sugar in pyridine and had m.p. 130-132° (from aqueous alcohol) and $[\alpha]_D^{24}$ –25.8° (butanone-2, c 2.82).

Found %: C 69.44, 69.14; H 7.21, 6.95. $C_{26}H_{31}O_6N$. Calculated %: C 68.85; H 6.89.

6-o-Anisylamino-6-desoxy-1,2:3,4-diisopropylidene-D-galactose (Id). A mixture of 1.5 g of Ts-DAG and 2.5 ml of o-anisidine was heated at 100° for 19 hr. The addition of ether formed a tarry precipitate of the salt (IId). The o-anisidine p-toluenesulfonate obtained (IId) had m.p. 151-152° after reprecipitation from ethyl acetate with ether and did not depress the melting point of an authentic sample.

Found: Equiv. 298.297. $C_7H_9ON \cdot C_7H_8O_3S$. Calculated: Equiv. 295.28.

The amino sugar was extracted from the ether with 1 N H_2SO_4, reprecipitated with NH_4OH, and purified by passing through a layer of Al_2O_3 in heptane. We obtained 0.35 g of pure (Id) with m.p. 65.5-66° (from aqueous alcohol) and $[\alpha]_D^{24}$ –93.5° (butanone-2, c 1.098).

Found %: N 4.06, 3.80. $C_{19}H_{27}O_6N$. Calculated %: N 3.83.

6-p-Anisylamino-6-desoxy-1,2:3,4-diisopropylidene-D-galactose (Ie). A mixture of 4.1 g of Ts-DAG and 1.85 g of p-anisidine was heated on a water bath for 10 hr. The compact solid mass formed was treated with ether and 2.0 g (91%) of p-anisidine p-toluenesulfonate separated. The salt was purified by reprecipitation from alcohol with ether and consisted of a slightly colored friable substance with m.p. 144-147°.

Found: Equiv. 294, 297. $C_7H_9ON \cdot C_7H_8O_3S$. Calculated: Equiv. 295.28.

The amino sugar was precipitated and purified on Al_2O_3 as described above. We obtained 1.4 g of colorless, lustrous crystals of (Ie) with m.p. 64-65.5° (from aqueous alcohol) and $[\alpha]_D^{24}$ –88.5° (butanone-2, c 2.7).

Found %: N 4.0, 3.82. $C_{19}H_{27}O_6N$. Calculated %: N 3.83.

The oxalate was obtained by the reaction of the amino sugar with anhydrous oxalic acid in ether and had m.p. 173-175°.

Found: Equiv. 218, 202. $C_{19}H_{27}O_6N \cdot (COOH)_2$. Calculated: Equiv. 227.71.

Investigation of Reaction Rates

Determination of reaction order. A mixture of 3.1003 g of Ts-DAG and 3.2194 g of p-toluidine was dissolved in butanol (b.p. 116.5-117°) and the solution made up to 54.2 ml (solution A). A 25-ml portion of solution A was diluted with exactly 25 ml of butanol (solution B). From buretts we transferred into test tubes 2-ml portions of solution A and 4-ml portions of solution B. Thus, the samples of solutions A and B contained the same amounts of starting materials.

The stoppered tubes were placed simultaneously in a stand on a boiling water bath. After definite time intervals, one tube each of mixture A and mixture B was taken from the bath and cooled, the contents were washed into beakers with water quantitatively, and the p-toluenesulfonic acid formed was titrated with KOH (0.0838 N) in the presence of phenolphthalein. Preliminary experiments showed that excess aromatic amine in the mixture did not affect the accuracy of the titrations. The experiments were carried out analogously with the other two solutions, which were prepared as follows: 2.600 g of Ts-DAG and 2.700 g of p-toluidine were dissolved in butanol and the solution made up to 54.3 ml (solution C): 24.5 ml of solution C was mixed with 3.6605 g of p-toluidine and diluted to 49 ml with butanol (solution D). The sample volumes were 2 ml for solution C and 4 ml for solution D. At the same time we carried out a blank experiment (without p-toluidine ; the correction for the blank experiment was ~0,1 ml of KOH solution and was deducted in the calculation of the data, which are given in Figs. 1 and 2.

The reaction rate constants were calculated from the differential equation (2), which differs from the normal equation for a bimolecular reaction [12] in the factor (a - 2x) instead of (a - x) (a is the amount of toluidine) since, as was pointed out above, 1 mole of Ts-DAG requires 2 moles of amine; one reacts while the second simultaneously binds the p-toluenesulfonic acid formed as the salt (II).

$$\frac{dx}{dt} = \frac{k_2}{v}(a - 2x)(b - x) \qquad (2)$$

$$k_2 = \frac{2.3}{t} \cdot \frac{v}{a - 2b} \cdot \lg \frac{b}{a} \cdot \frac{a - 2x}{b - x} \qquad (3)$$

a is the amount of p-toluidine in the sample, b is that of Ts-DAG; x is that of the salt (II) formed; v is the sample volume (ml).

According to [12], integration of (2) leads to equation (3) and k_2 was calculated from the latter (Table 2).

Comparison of rates of reaction of Ts-DAG with different amines.* Into test tubes we placed two samples of each of the 16 amines investigated [$9.26 \cdot 10^{-4}$ (±2-3%) mole portions] and 2-ml portions of a butanol solution of Ts-DAG ($2.3 \cdot 10^{-4}$ mole per portion). All the tubes were simultaneously heated on a boiling water bath for 8.5 hr and then the p-toluenesulfonic acid content was determined as described. We allowed for data from blank experiments in the calculations. The results are given in Table 1.

SUMMARY

1. A method was developed for synthesizing N-arylaminodesoxy sugars by the reaction of 6-tosyldiacetone-D-galactose and aromatic amines.

2. It was found that this reaction follows an equation of the 2nd order. The reaction rate is higher, the higher the basicity of the amine used.

3. It was concluded that the formation of aminodesoxy sugars from sulfonic esters proceeds by an S_N2 mechanism.

LITERATURE CITED

1. J. H. Hodge, Adv. carbohydr. chem. 10, 169 (1955).
2. a) B. R. Baker et al., J. Am. Chem. Soc. 80, 6577 (1958); b) N. S. Tikhomirova-Sidorova and G. E. Ustyuzhanin ZhOKh 28, 3210 (1958); c) R. Kuhn et al., Lieb. Ann. 602, 217 (1957); d) P. F. Lloyd, M. Stacey, Tetrahedr. 9, 116 (1960).
3. Ch. Hodgman et al., Handbook of chem. and phys., 1642, 38 ed. (1956-1957).
4. N. Hall, J. Am. Chem. Soc. 52, 5115 (1930).
5. Steric Effects in Organic Chemistry, Collection [Russian translation] IL, 573 (1960).
6. A. Vin'eron, Processing Results of Physicochemical Observations [in Russian], 129, M., ONTI (1936); M. S. Zakhar'evskii, Kinetics of Chemical Reactions [in Russian] 9. Izd. LGU (1959).
7. A. C. Cope, T. Y. Shen, J. Am. Chem. Soc. 78, 3177 (1956).
8. R. U. Lemieux, J. Am. Chem. Soc. 80, 4745 (1958); M. L. Wolfrom et al., J. Am. Chem. Soc. 81, 3716 (1959).
9. C. K. Ingold, Reaction Mechanism and Structure of Organic Compounds [Russian translation] M., IL, 305 (1959); T. I. Temnikova, Course in the Theoretical Bases of Organic Chemistry [in Russian] L., GKhI, 272 (1959).
10. A. L. Raymond, E. F. Schroeder, J. Am. Chem. Soc. 70, 2788 (1948); A. B. Foster et al., J. Am. Chem. Soc. 1949, 2545.
11. Beilst., XII.
12. A. V. Rakovskii, Introduction to Physical Chemistry [in Russian] M., ONTI, 574 (1938).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

---

*The students G. Fridman, N. Denisova, and P. Yakovlev helped with the experiments.

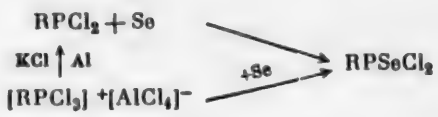
SYNTHESIS OF DIACID CHLORIDES OF ALKYLSELENOPHOSPHINIC ACIDS

S. Z. Ivin and I. D. Shelakova

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4052-4053, December, 1961
Original article submitted January 23, 1961

The only acid halides of selenium derivatives of phosphorus acids described in the literature are the acids chlorides and bromides of diaroxy-phosphoric acids, which were synthesized by the addition of selenium to the corresponding acid halide of a diaroxyphosphorous acid [1]. In analogy with the synthesis of acid halides of diaroxyselenophosphoric acids, we proposed to synthesize the diacid chlorides of alkylselenophosphinic acids by the addition of selenium to alkyldichlorophosphines. However, during vacuum distillation of the reaction mixture, selenium was deposited as a red precipitate and there distilled a complex mixture which consisted mainly of diacid chlorides of alkylselenophosphinic and alkylphosphinic acids and which was very difficult to separate. It was possible to isolate the diacid chlorides of the alkyl-selenophosphinic acids formed by vacuum distillation in a stream of nitrogen. In this way we obtained the diacid chlorides of methyl- and ethylselenophosphinic acids.

We developed a new method of synthesizing the diacid chloride of ethyl-selenophosphinic acid, which consisted of the reaction of metallic selenium with the complex compound of ethyl chloride, phosphorus trichloride, and aluminum chloride. If the starting alkyldichlorophosphines in the first method are obtained by reduction of these complexes [2], then both methods of synthesizing diacid chlorides of alkylselenophosphinic acids may be represented by the scheme:



The latter reaction proceeds and gives the expected product only in a stream of nitrogen. When the reaction flask contains air or oxygen, selenium separates as a red precipitate and a complex mixture is formed from which it is not possible to isolate the diacid chloride of the alkylselenophosphinic acid.

The diacid chlorides of alkylselenophosphinic acid are unstable and readily liberate selenium in contact with air. The substances can be stored for a long time in a nitrogen atmosphere or in sealed ampoules.

EXPERIMENTAL

Diacid chloride of methylselenophosphinic acid. Into a Claisen flask with a pear fractionating head and a distillation condenser were placed 83 g of methyldichlorophosphine and 56 g of powdered selenium. The reaction mixture was then heated to 80°. The diacid chloride of methylselenophosphinic acid formed was vacuum distilled (the addition of the selenium and distillation of the substance formed were performed in a stream of nitrogen). We obtained 80 g (67%) of the product.

B. p. 74-75° at 25 mm, d_4^{18} 1.7540, n_d^{18} 1.5970.

Found %: P 16.05; Cl 36.45; Se 39.6. CH_3Cl_2PSe. Calculated %: P 15.7; Cl 36.0; Se 40.5.

Diacid chloride of ethylselenophosphinic acid. The synthesis was carried out as described above with 58 g of ethyldichlorophosphine and 35 g of selenium. We obtained 60 g (65%) of the substance.

B. p. 92-94° at 25 mm, d_4^{24} 1.6750, n_D^{24} 1.5850.

Found %: P 15.1; Cl 34.15; Se 37.4. $C_2H_5Cl_2PSe$. Calculated %: P 14.7; Cl 33.6; Se 38.0.

Diacid chloride of ethylselenophosphinic acid from complex and selenium. Into a Claisen flask with a distillation condenser was placed a mixture of 50.0 g (0.15 mole) of the complex compound of ethyl chloride, phosphorus trichloride, and aluminum chloride, 11.7 g (0.15 g-at.) of selenium, and 11.1 g (0.15 mole) of freshly calcined potassium chloride. The mixture was shaken thoroughly, kept in a stream of nitrogen for 1 hr, and then heated to 200°, when the complex melted. The diacid chloride formed was distilled at 40-50 mm and 100-130°. Redistillation gave 15.6 g (50%) of the diacid chloride.

B.p. 95° at 20 mm, d_4^{20} 1.6800, n_D^{20} 1.5850.

Found %: P 15.06; Cl 33.7; Se 35.85. $C_2H_5Cl_2PSe$. Calculated %: P 14.7; Cl 33.8; Se 37.6.

SUMMARY

1. The diacid chlorides of methyl- and ethylselenophosphinic acids were synthesized.

2. A new method was developed for the synthesis of the diacid chloride of ethylselenophosphinic acid, based on the reaction of metallic selenium with the complex compound of ethyl chloride, phosphorus trichloride, and aluminum chloride.

LITERATURE CITED

1. Streeker, Grossman, Ber. 49, 63 (1916).
2. I. P. Komkov, K. V. Karavanov, and S. Z. Ivin, ZhOKh 28, 2963 (1958).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

NEW METHOD OF SYNTHESIZING PHOSPHINIC AND THIO-PHOSPHINIC ESTERS

XXXVI. SYNTHESIS OF PHOSPHINIC ACID DERIVATIVES WITH CYCLIC RADICALS IN THE ESTER GROUPS

A. N. Pudovik and G. P. Krupnov

Kazan' Branch of the All-Union Motion Picture Scientific Research Institute

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4053-4055, December, 1961
Original article submitted December 26, 1960

Phosphoric esters containing aromatic radicals, namely, triphenyl phosphate and tricresyl phosphate, are used widely as plasticizers for cellulose esters and various polymeric materials. It may be surmised that phosphinic and thiophosphinic esters containing cyclic radicals in the ester groups should also have good plasticizing properties. To synthesize compounds of this type we used the addition of partial esters of phosphorus acids, namely, dicyclohexylphosphorous, dibenzylphosphorous, and diphenylphosphorous acids, to various unsaturated compounds of the electrophilic type. The addition of dicyclohexylphosphorous and dibenzylphosphorous to acrylonitrile, acrylic and methacrylic esters, and Schiff's bases proceeds very readily in the presence of alkali metal alcoholates [1]. However, the distillation of the addition products presents considerable difficulties. Even when high vacuum was used, in a number of cases the addition products were obtained in low yields because of partial decomposition and resinification of the reaction mixture during distillation. The constants of the products obtained are given in Table 1. The esters and nitriles of dibenzylphosphono- and dicyclohexylphosphonopropionic and isobutyric acids are colorless viscous liquids, which are insoluble in water, but soluble in most organic solvents. They are quite resistant to light and heating and have a low volatility.

The characteristics of the products from addition to anils are given in Table 2. These crystalline substances are insoluble in water and soluble in alcohol.

TABLE 1. Esters and Nitriles of Phosphono Carboxylic Acids $(RO)_2\overset{O}{\overset{\|}{P}}CH_2CH(R')X$

R	R'	X	Yield (%)	Boiling Point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		%P	
							Found	Calcu.	Found	Calcu.
C_6H_{11}	H	CN	13.6	120–124° (0.01)	1.4770	1.0860	77.82	77.75	10.05	10.4
C_6H_{11}	H	$COOCH_3$	27	174–176 (7–8)	1.4570	1.0730	84.59	84.20	9.37	9.36
C_6H_{11}	CH_3	$COOCH_3$	68	190–193 (3)	1.4740	1.0960	88.76	88.82	9.44	9.12
C_6H_{11}	CH_3	$COOC_4H_9$	63	193–196 (1)	1.4690	1.0580	102.58	102.20	8.06	7.97
$C_6H_5CH_2$	H	CN	29	160–162 (0.001)	1.5270	1.1530	84.20	84.22	9.80	9.53
$C_6H_5CH_2$	H	$COOCH_3$	24	143–145 (0.001)	1.5030	1.1382	90.55	90.64	8.73	8.90
$C_6H_5CH_2$	CH_3	$COOCH_3$	33	150–153 (0.001)	1.5272	1.1450	94.73	95.15	8.67	8.79
$C_6H_5CH_2$	CH_3	$COOC_4H_9$	51	169–172 (0.001)	1.5100	1.1010	109.2	109.6	7.73	7.54

Because of the difficulty of distilling dibenzylphosphorous acid itself, it was used in an undistilled state in addition experiments. The addition proceeded at a high rate in the presence of sufficient catalyst. It was also shown that addition products could be obtained in quite a pure form without distillation in high vacuum. In this case the reaction products were washed several times with water and dried in ether solution over calcium chloride or in a desiccator over phosphorus pentoxide. The constants of the addition products obtained in this way were very

TABLE 2. Esters of Aminophosphinic Acids $(RO)_2\overset{O}{\overset{\|}{P}}CH(C_6H_5)NHC_6H_4X$

R	X	Yield (%)	Melting Point	% P	
				Found	Calculated
C_6H_{11}	p-CH_3	86	83—85°	6.91	6.70
C_6H_{11}	H	61	89—90	8.02	7.56
C_6H_{11}	p-NO_2	64	141—143	6.32	6.57
C_6H_5	H	82	150—152	7.34	7.73
C_6H_5	p-CH_3	88	170—171	6.91	7.20
$C_6H_5CH_2$	H	73	109—110	7.00	6.68

close to those of the products obtained by vacuum distillation. In the addition of diphenylphosphorous acid, satisfactory results were obtained only with anils. Addition occurred with acrylic and methacrylic esters, but it was impossible to isolate the products in a pure form. Gradual decomposition and resinification occurred during vacuum distillation. The characteristics of the products obtained are given in Table 2.

EXPERIMENTAL

Dicyclohexylphosphorous and dibenzylphosphorous acids were prepared by the method described in [2] and diphenylphosphorous acid by the method described in [3].

Reaction procedure. To a mixture of the unsaturated compound and partial ester of phosphorous acid, in equimolecular amounts, was added a solution of sodium alcoholate in anhydrous alcohol dropwise with continuous stirring. The alcoholate was added at such a rate that the temperature of the reaction mixture rose slowly to 50-90°. The reaction mixture was heated on a water bath for 1 - 2 hr. It was then treated by one of two methods: a) the reaction mixture was distilled at normal pressure or more often, in high vacuum; b) the reaction mixture was washed repeatedly with water to remove the catalyst and the product dried in ether solution over calcium chloride or in a vacuum desiccator over phosphorus pentoxide.

SUMMARY

It was shown that dicyclohexylphosphorous, dibenzylphosphorous, and diphenylphosphorous acids add in the presence of an alkaline catalyst to unsaturated compounds of the electrophilic type, namely, esters and nitriles of unsaturated carboxylic acids and Schiff's bases to form esters and nitriles of phosphono carboxylic acids and esters of aminophosphinic acids.

LITERATURE CITED

1. A. N. Pudovik, Usp. Khim. 22, 547 (1954).
2. Atherton, Koward, A. Todd, J. Chem. Soc. 1948, 1182.
3. A. E. Arbuzov and M. Imaev, Izv. AN SSSR, OKhN 1959, 171.

LETTERS TO THE EDITOR

SOME REACTIONS OF HETEROORGANIC COMPOUNDS OF GROUP IV CATALYZED BY ALUMINUM CHLORIDE

G. A. Razuvaev, N. S. Vyazankin, O. S. D'yachkovskaya, I. G. Kiseleva, and Yu. I. Dergunov

Scientific Research Institute of Chemistry at N. I. Lobachevskii Gor'kii State University

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, p. 4056, December, 1961
Original article submitted July 3, 1961

We reported previously that the action of iso-C_3H_7Cl on $(C_2H_5)_4Si$ or $(C_2H_5)_4Sn$ in the presence of $AlCl_3$ gave high yields of $(C_2H_5)_3SiCl$ and $(C_2H_5)_3SnCl$ [1]. This reaction may be used for the synthesis of $(C_2H_5)_3MX$ (M=Si, Ge, Sn; X=Cl and Br), and also $(C_2H_5)_5Si_2Br$.

To $(C_2H_5)_4M$, containing ≃ 2 wt. % of Cl_3, was added an equimolecular amount of iso-C_3H_7X dropwise; the mixture was heated until the evolution of gaseous products ceased (~4 hr). The gaseous products consisted of 7-10% of ethane, 35-45% of ethylene, 42-54% of propane, and 1-3% of a propylene–butane fraction. Fractionation yielded a small amount of isopentane and $(C_2H_5)_3MX$.

$(C_2H_5)_3MX$	Yield (%)	Boiling point (pressure in mm)	n_D^{20}	Notes
$(C_2H_5)_3SnBr$	70.4	104—107° (15)	1.5225	Synthesis carried out with the add. of 2 ml of C_6H_6
$(C_2H_5)_3SiBr$	93.1	159—164	1.4559	
$(C_2H_5)_3GeBr$	86.6	187—191	1.4862	
$(C_2H_5)_3GeCl$	60.0	173—177	1.4650	
$(C_2H_5)_5Si_2Br$	72.2	88 (2)	1.4860	Found %: Br 27.71. $C_{10}H_{25}Si_2Br$. Calculated %: Br 28.40

$(C_2H_5)_5Si_2Br$ was converted into decaethyltetrasilane by treatment with highly disperse molten sodium according to the data in [2]. The yield was 20.2%.

B.p. 164–170° (1 mm), n_D^{20} 1.5160.
Found %: C 59.46; H 12.44. M 385. $C_{20}H_{50}Si_4$. Calculated %: C 59.63; H 12.51; M 402.8.

It was also established that hexaethyldisilane, like the Sn and Pb analogs [1], disproportionates according to the equation $2(C_2H_5)_6Si_2 \rightarrow 3(C_2H_5)_4Si+Si$ when heated to 235° with 3-5 wt. of $AlCl_3$.

LITERATURE CITED

1. G. A. Razuvaev, N. S. Vyazankin, Yu. I. Dergunov, O. S. D'yachkovskaya, DAN SSSR 132, 364 (1960).
2. H. Gilman, R. K. Ingham, A. G. Smith, J. Org. Ch. 18, 1743 (1953).

PHOTOREACTION OF CARBON TETRACHLORIDE WITH DIOXANE

G. A. Razuvaev, N. S. Vasileiskaya, V. T. Bychkov, and A. E. Makar'eva

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12, pp. 4057-4058, December, 1961
Original article submitted July 8, 1961

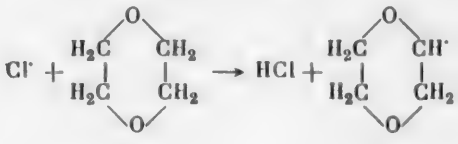
Continuing the investigation of photoreactions of polyhalogen compounds with alcohols, we decided to carry out the reaction of carbon tetrachloride with dioxane. Pfordte [1] showed that when irradiated with ultraviolet light under nitrogen, dioxane loses hydrogen and the dioxanyl radicals formed dimerize to give bidioxanyl. The latter was found previously [2] in the photolysis of diphenylmercury in dioxane. In this case, the dioxanyl radicals, which then dimerized, were obtained by the abstraction of hydrogen from dioxane by phenyl radicals.

We showed that when a mixture of CCl_4 (0.7 mole) and dioxane (0.4 mole) was irradiated with ultraviolet light for 100 hr there was abstraction of hydrogen by chlorine, and to a small extent, CCl_3 radicals. From the reaction products we isolated HCl (0.1 mole), chloroform (0.001 mole), hexachloroethane (0.005 mole), and a solid substance with m.p. 136-138°, which was soluble in water and readily soluble in dioxane, ether, and dioxane. It was sparingly soluble in benzene, carbon tetrachloride, cyclohexane, and heptane, contained 51.29% of chlorine, and had a molecular weight of 219. This makes it possible to assign to it the formula $C_5H_7O_2Cl_3$ (calculated Cl 51.83%; M 205).

A positive isonitrile reaction indicated the presence of a CCl_3 group, and cleavage by 2,4-dinitrophenylhydrazine hydrochloride to form glyoxal 2,4-dinitrophenylhydrazone [3] indicated the presence of a dioxane ring. The infrared spectrum of this compound showed that it contained a dioxane ring and also a C—Cl bond [4,5]. All these data indicate that the substance was trichloromethyldioxane.

On the basis of the products isolated, we proposed the following reaction scheme:

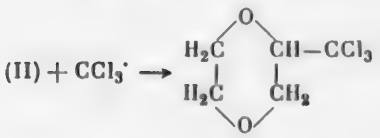
$$CCl_4 + h\nu \longrightarrow CCl_3^{\cdot} + Cl^{\cdot}$$



(I) (II)

$$(I) + CCl_3^{\cdot} \longrightarrow CHCl_3 + (II)$$

$$2CCl_3 \longrightarrow C_2Cl_6$$



We did not isolate the dimerization product of dioxanyl radicals, i.e., bidioxanyl. Likewise, we did not isolate chlorodioxane, which could have been formed by the abstraction of chlorine from carbon tetrachloride by the dioxanyl radical.

LITERATURE CITED

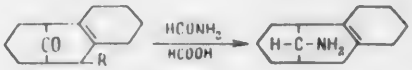
1. K. Pfordte, Lieb. Ann. 625, 30 (1959).
2. G. A. Razuvaev, N. R. Novotorov, Uch. zap. GGU 17, 125 (1951).
3. W. Casse, J. Am. Chem. Soc. 69, 500 (1947).
4. D. A. Ramsay, Proc. Roy. Soc. (Lond.) A 190, 562 (1947).
5. Application of Spectroscopy in Chemistry. Edited by West [Russian translation] IL (1950).

CONVERSION OF TRICYCLOHEXENONES TO TRICYCLOHEXENYLAMINES

M. N. Tilichenko, N. S. Barbulescu, and V. I. Vusotskii

Far Eastern State University
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4058-4059, December, 1961
Original article submitted April 24, 1961

The Leuckart reaction has not been applied previously to unsaturated carbonyl-bridge compounds. By treatment of tricyclohexenone (I)[1,2]and methyl tricyclohexenone (II) [3-5], which were prepared and described previously, with formamide and formic acid under the conditions of this reaction we obtained the corresponding primary amines (III) and (IV). This type of amine with an amino group at the bridge carbon has not been described in the literature.



(I) R = H, (III) R = H,
(II) R = CH_3, (IV) R = CH_3.

Tricyclohexenylamine [9-amino-2,3-tetramethylenebicyclo-(3,3,1)-nonene-2,3] (III) had b.p. 137 – 139° (8 mm), d_4^{20} 1.0282, n_D^{20} 1.5358.

Found %: N 7.31, 7.49. M 199, 193. $C_{13}H_{21}N$. Calculated %: N 7.23. M 191.

N-Formyltricyclohexenylamine had m.p. 146.5° (from 70% alcohol) and gave (III) on alkaline hydrolysis.

Found %: N 6.34, 6.53. $C_{14}H_{21}ON$. Calculated %: N 6.33.

N-Benzylidenetricyclohexenylamine was formed readily by mixing the amine with benzaldehyde and had m.p. 82.7°.

Found %: N 5.22. $C_{20}H_{25}N$. Calculated %: N 5.01.

Methyltricyclohexenylamine [9-amino-2-methyl-3,4-tetramethylenebicyclo-(3,3,1)nonene-3,4] (IV) had b.p. 154 – 155° (1 mm), d_4^{20} 1.0151; n_D^{20} 1.5320.

Found %: N 6.70. $C_{14}H_{23}N$. Calculated %: N 6.76.

N-Acetylmethyltricyclohexenylamine had m.p. 144 – 146° (from dioxane).

Found %: N 5.64. $C_{16}H_{25}ON$. Calculated %: N 5.62.

The amines were characterized by their infrared spectra. Bands of a primary amino group (3500-3300 and 1634 cm^{-1}) were found.

The double bond in the amines obtained was detected by the same reactions as in the case of compounds (I) and (II), for example, Deniges reagent.

LITERATURE CITED

1. M. N. Tilichenko, Saratov University Yearbook [in Russian] 1954, 502; Uch. zap. SGU 71, vyp. khim. 1959, 153.
2. S. Julia, D. Varech, C. R. 246, 1559 (1958).

3. M. N. Tilichenko, N. S. Barbulescu, Saratov University Yearbook [in Russian] 1954, 510.
4. N. Barbulescu, G. Apostolache, Revista de Chem. 1955, 101.
5. J. Plesek, P. Munk, Coll. Cz. chem. Commun. 22, 1596 (1957).

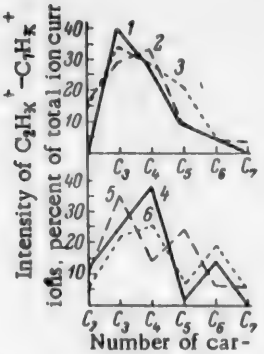
All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

SOME RULES IN THE MASS SPECTRA OF MONOOLEFINS

A. A. Polyakova and R. A. Khmel'nitskii

Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4059-4060, December, 1961
Original article submitted April 28, 1961

An examination of published [1] mass spectra showed that the specificity of dissociative ionization of different hydrocarbon groups is characterized not only by the formation of homologous series of fragment ions, but also by the distribution of the ion intensities in the mass spectra relative to the number of carbon atoms: the position of the maximum on the distribution curve depends on the number of multiple bonds in the molecule and as the latter accumulate, the maximum is displaced toward heavier ions [2]. Together with this, the distribution curves reflect differences in the structure of isomers of a given group. The dissociation of cyclopentanes and cyclohexanes forms approximately equal amounts of the ions $C_3H_X^+$ and $C_4H_X^+$, but substantially different amounts of the ions $C_5H_X^+$, and this is used to determine them in mixtures.



Ion intensity distribution relative to number of carbon atoms for different types of monoolefins. The number on the curves correspond to those in the table.

A study of the mass spectra of monoolefins showed that the nature of the ion intensity distribution relative to the number of carbon atoms depends on the position of the double bond and the structure of the carbon skeleton (see table and figure).

Alkenes with a carbon chain of normal structure have one maximum on the distribution curve corresponding to the ions $C_3H_X^+$ for 1- and 3-alkenes and to the ions $C_4H_X^+$ for 2- and 4-alkenes.

As the degree of branching of the carbon skeleton of isoolefins increases, the form of the distribution curves changes. For mono- and dialkyl-1-alkenes, approximately equal amounts of the ions $C_3H_X^+$, $C_4H_X^+$ and $C_5H_X^+$ are formed. On the distribution surves for trimethyl-1-alkenes, in addition to the maximum for $C_4H_X^+$ ions, there appears a second maximum corresponding to the ions $C_6H_X^+$ Monomethyl-2- and 3-alkenes have two maxima for $C_3H_X^+$ and $C_5H_X^+$. The maxima for dimethyl- and trimethyl-2-alkenes correspond to the ions $C_4H_X^+$. and $C_6H_X^+$.

These observations may be used as a basis for identifying types of olefin by mass spectra.

No.	Type of monoolefin	Ion intensity (% of total ion current)					
		$C_2H_X^+$	$C_3H_X^+$	$C_4H_X^+$	$C_5H_X^+$	$C_6H_X^+$	$C_7H_X^+$
1	1- and 3-n-Alkenes	1.0	40.1	28.0	10.0	7.0	2.0
2	2- and 4-n-Alkenes	15.0	29.0	33.0	10.0	5.0	3.0
3	Mono- and dimethyl-1-alkenes	14.5	34.5	29.0	21.0	5.0	0.0
4	Trimethyl-1-alkenes	12.7	25.0	39.0	2.0	15.0	0.0
5	Monomethyl-2- and 3-alkenes	11.0	35.0	14.0	24.0	6.6	5.8
6	Di- and trimethyl-2-alkenes	10.4	22.6	26.0	7.0	20.0	5.2

LITERATURE CITED

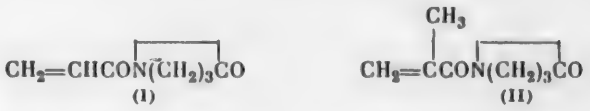
1. American Petroleum Institute Research Project 44, Mass Spectral Data, N. Y. (1952); A. A. Polyakova, K. I. Zimina, A. A. Petrov, R. A. Khmel'nitskii, DAN SSSR 127, 386 (1959); ZhOKh 30, 912, 2977 (1960).
2. A. A. Polyakova, K.I. Zimina, R. A. Khmel'nitskii, Conference on Organic Analysis 1961. Abstracts of proceedings [in Russian] Izd. MGU, 160 (1961).

ACRYLYL- AND METHACRYLYLPYRROLIDONES

F. P. Sidel'kovskaya, M. G. Zelenskaya, and M. F. Shostakovskii

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
Translated from Zhurnal Obshchei Khimii, Vol 31, No 12,
pp. 4060-4061, December, 1961
Original article submitted July 10, 1961

Together with the esters of acrylic and methacrylic acids, the amides of these acids have recently attracted considerable attention as new monomers for the synthesis of high-molecular compounds. Derivatives of acrylic and methacrylic acids and a cyclic amide, pyrrolidone, were prepared for the first time in the present work.



(I) (II)

In a number of cases, the introduction of a lactam ring into the molecules of organic compounds increases their solubility, dissolving power, and tendency to form complexes. By the action of acrylyl and methacrylyl chlorides on the sodium derivative of pyrrolidone (in the presence of the inhibitor propylgallate) at -10 to 15° we synthesized acrylylpyrrolidone (I) (~20% yield) and methacrylylpyrrolidone (II) (~40% yield).

Acrylylpyrrolidone (I) was a mobile liquid:

b.p. 55 – 58° (3 · 10^{-3} mm), d_4^{20} 1.1413, n_D^{20} 1.5045, MR_D 36.13; calcu. 35.82.
Found %: C 59.87, 59.96; H 6.59, 6.58; N 9.69, 9.59. $C_7H_9O_2N$. Calculated %: C 60.42; H 6.52; N 10.07.

Methacrylylpyrrolidone (II) formed white crystals:

b.p. 127 – 130° (1.5 mm) and m.p. 24 – 25°.
Found %: C 62.67, 62.89; H 7.33, 7.25; N 9.09, 9.19. $C_8H_{11}O_2N$. Calculated %: C 62.72; H 7.23; N 9.14.

The structure of the compounds synthesized was confirmed by the infrared spectra, in which we found characteristic absorption bands of the CO group and a terminal double bond.

Acrylylpyrrolidone polymerized very readily: even during its synthesis and distillation it formed a solid polymer, which was insoluble in water and organic solvents. Methacrylylpyrrolidone was less active in polymerization: a polymer of (II) was obtained in 20% yield by heating the monomer at 60° for 30 hr in the presence of 5% of azoisobutyronitrile. This was a white powder (m.p. ~270°), which was soluble only in dimethylformamide.

The properties of the monomers and polymers synthesized and also the possibility of synthesizing acrylyl and methacrylyl lactams from piperidone and caprolactam are being studied.

DISCUSSION

NATURE OF SI – O BONDS AND INTERATOMIC DISTANCES IN SILICATES

A. N. Lazarev

Institute of Silicate Chemistry, Academy of Sciences, USSR
Translated from Zhurnal Obshchei Khimii, Vol. 31, No. 12,
pp. 4061-4062, December, 1961
Original aritcle submitted July 6, 1961

In a recent communication, M. G. Voronkov [1] discussed the nature of Si – O bonds in silicates from the point of view of the participation of $d\pi - p\pi$ interaction in the formation of these bonds and the resultant differences in the order of bonds of the type Si – O and Si – O(Si) and also pointed out the effect of interionic interactions on the redistribution of $d\pi - p\pi$ bonds in the silicon-oxygen anion. The author based these considerations on literature data on interatomic distances in silicates.

However, most of the interatomic distances given in M. G. Voronkov's work were taken from x-ray structural investigations of the thirties and cannot be used as a basis for discussing the nature of the bond as they are too inaccurate. Moreover, in a number of cases the interatomic distances used were from work that is known to be inaccurate or unreliable. Thus, 1.48 and 1.76 A were given for the distances $r_{Si-O(Si)}$ for wollastonite [2], although the model of the cyclic anion (Si_3O_9) adopted in this work was disproved by the work of N. V. Belov [3] and Liebau [4]. For hardystonite the author used doubtful data from [2], in which the centrosymmetry of the groups Si_2O_7 was assumed (as yet there are no accurate data on the structure of this mineral, but the SiOSi angle has been estimated at about 145° spectroscopically [5]). The distances given for all the compounds are those which differ most from the mean values for the Si– O^- and Si– O (Si) bonds [2]. For example, of the four distances for diopside ($r_{Si-O(Si)}$ 1.59 and 1.76 A and r_{Si-O^-} 1.54 and 1.64 A), two are given, namely, 1.76 and 1.54 A, and of the three distances for hardystonite r_{Si-O^-} 2 × 1.64, 1.54 A, the last was selected. Quite improbable values for the distances between silicon and oxygen are given for vesuvian, namely, 1.86 and 1.28 A.

When we turn to the data of modern precision x-ray structural investigations there is normally a substantial decrease in the difference in the Si– O bond lengths. For example, M. G. Voronkov gives the distances of 1.51 and 1.80 A for natrolite [2], while according to modern data, the Si– O distances in this mineral are from 1.60 ± 0.02 to 1.64 ± 0.02 A [6].

Apart from the unreliability of the data on interatomic distances on which M. G. Voronkov based his statement on the existence of double bonds between silicon and oxygen in silicates, there are other considerations according to which the ratio of the orders of the bonds Si– O^- and Si – O (Si) does not exceed ~ 1.3. Firstly, a considerable part of the minerals examined by M. G. Voronkov are pyro- or metasilicates, which contain three or two (in most cases equivalent) Si – O^- bonds, respectively, at each silicon atom. It has been pointed out in the literature [7] that there cannot be appreciable $d\pi - p\pi$ interaction in several Si – O bonds at one silicon atom.

Secondly, even in the most favorable cases, spectroscopic data (more sensitive to a change in the nature of bonds than interatomic distances) do not show bonds with an order of about 2. One such example is talc with lamellar "2-dimensional" anions, i.e., with bonds of the type $[(Si)O]_3Si-O^-$. A comparison of the observed frequencies with calculations for the vibrations of a planar lattice [8] leads to a ratio $\frac{k_{Si-O^-}}{k_{Si-O(Si)}}$ of about 1.2 or 1.3. It can be assumed therefore that even under optimal conditions, the overlapping of the 3d orbitals of the Si atoms and 2p orbitals of the O atoms is insufficient for the formation of a π-bond, though it is approximately equivalent to a σ-bond. (A detailed discussion of the spectra of talc and other silicates with lamellar anions will be published in the journal "Optika i Spektroskopiya.")

From what has been stated it follows that the basic premises of M. B. Voronkov's work, namely, the very wide range of Si– O^- and Si– O(Si) distances in the structures of silicates (from 1.5 to 1.8 A) and an equally wide range of changes in the order of Si– O bonds is not confirmed experimentally. As regards the existence of differences in lengths of Si– O^- and Si– O(Si) bonds, it has already been pointed out repeatedly in the literature [9,10]. In [9],

the difference in the Si– O^- and Si– O(Si) distances in pyrosilicates was even used as a criterion for estimating the reliability of some x-ray structural investigations.

The effect of interionic interactions on the redistribution of $d\pi - p\pi$ bonds in a silicon– oxygen anion was evidently pointed out for the first time by Ya. I. Ryskin [11] on the example of O_3SiOH groups.

LITERATURE CITED

1. M. G. Voronkov, DAN SSSR, 138 106 (1961).
2. Strukturbericht, 1928 –1936.
3. Kh. S. Mamedov, N. V. Velov, DAN SSR 107, 463 (1956).
4. Dornberger-Schiff, F. Liebau, E. Thilo, Acta Crystallogr. 8, 752 (1955).
5. A. N. Lazarev, Opt. i spektr. 9, 195 (1960).
6. W. M. Meier, Z. Kristallogr. 113, 430 (1960).
7. G. Dzhaffe, Usp. khim. 26, 1060 (1957).
8. B. I. Stepanov, A. M. Prima, Opt. i spektr. 4, 734; 4, 15 (1958).
9. G. A. Barclay, E. G. Cox, Z. Crystallogr. 113, 23 (1960).
10. D. E. C. Corbridge, Acta Crystallogr. 9, 308 (1956).
11. Ya. I. Ryskin, Opt. i spektr. 4, 532 (1958); 7, 278 (1959).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

PREPARATION OF MONOSACCHARIDE DERIVATIVES IN THE FURANOSE FORM

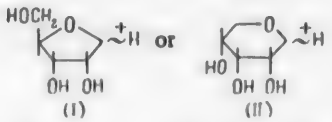
A. A. Abramzon and M. V. Ostrovskii

Translated from Zhurnal Obshchei Khimii, Vol. 31, No.12,
pp. 4062-4064, December, 1961
Original article submitted February 23, 1961

Great attention is being paid to the synthesis of furanoses at the present time, especially in connection with the synthesis of nucleosides. One of the most important reactions for the preparation of furanoses is Fischer's reaction for the preparation of glycosides. Shafizadeh [1] explained the formation of furanoses in this reaction by the fact that closure of the more stable six-membered ring requires a special position and orientation of C_5 as well as the other carbon atoms; thus, the formation of a six-membered ring is less probable than a five-membered ring, especially at low temperature. However, this does not explain the differences in the reactions of monosaccharides with alcohols (Fischer's reaction) and with amines and urea (formation of pyranosides) and other characteristics of the reactivity of monosaccharides. Below we give a mechanism which is more probable from our point of view.

It is generally accepted that in solutions of sugars the equilibrium is strongly displaced toward the pyranose form [2]. In the reactions of sugars with electrophilic agents (acetylation, benzoylation, nitration, etc.), in which the reagent reacts with hydroxyl groups without touching the atoms of the ring, derivatives with a pyranose ring are formed at low temperatures and the formation of considerable amounts of furanoses is observed at higher temperatures [3]. This indicates that the pyranose form of sugars is more favorable energetically than the furanose form. However, in the Fischer reaction, glycosides are obtained in the furanose form in a number of cases.

In this reaction, alcohol is the nucleophilic agent and carbon atom 1 of the aldose is the electrophilic agent. The reaction evidently proceeds by an S_N1 mechanism through the formation of a carbonium ion, which is catalyzed by hydrochloric acid.



or

(I) (II)

The possibility of the existence of such ions was postulated in [4]. It is known [5] that the C– H or C– OH bonds in five-membered rings have an energetically unfavorable eclipsed conformation (strain of 4-6 kcal / mole) and in six-membered rings a more energetically favorable canted conformation (strain of 0.9 kcal/ mole). In the formation of a carbonium ion in a five-membered ring, one carbon atom with a coordination number of 3 is formed and two eclipsed conformations disappear. In the formation of a carbonium ion in a six-membered ring, this gain in energy is not obtained and the carbon with the coordination number of 3 and valance angles of 120° makes the six-membered ring more strained [6]. From the above it follows that the formation of a carbonium ion in a furanose must proceed more readily than in a pryranose and the furanose form must react more energetically by an S_N1 mechanism than the pyranose form. As the furanose is removed, the equilibrium is displaced toward the formation of new portions of furanose.

A reaction by an S_N2 mechanism would proceed at a lower rate, but analogously to the above as the intermediate complex in this reaction contains carbon with valence angles of 120° [7]. However, Shafizadeh [1] presents evidence against an S_N2 mechanism.

The electrophilicity of the monosaccharide molecule alone is inadequate for the formation of furanosides as it is well known that the action of such nucleophilic agents as amines and urea on monosaccharides yields amino sugars with six-membered rings [8] and it is only the action on monosaccharides of such weak nucleophilic agents as alcohols which yields glycosides with a five-membered ring. This is explained by the fact that under treatment with strong nucleophilic agents, both the active furanose and the less active pyranose react; as a result of this there is a competing reaction in accordance with the law of mass action and a predominant amount of the pyranoside is obtained. In a reaction with weak nucleophilic reagents, the more active furanose form reacts predominantly.

In addition, a strong nucleophilic agent may bind the catalyst (acid) and then the reaction may proceed by an S_N2 mechanism or require more drastic reaction conditions.

Two further facts shed light on the mechanism of the formation of glycosides and the conditions for the formation of furanosides: 1) in the preparation of glycosides at high temperatures, pyranosides are obtained as the main products; 2) treatment of ribose with a 1% solution of hydrogen chloride in methanol yields furanosides, while 2-desoxyribose yields α- and β-methyl-2-desoxypyranosides. If a 0.1% solution of hydrogen chloride is used in the latter case, a methyl-2-desoxyribofuranoside is obtained [9]. This is explained by the fact that for desoxyribose, the difference in the reaction rates of the pyranose and furanose forms will be less because of the replacement of one bulky hydroxyl group by hydrogen. Consequently, there is a decrease in the strain and the difference in the activation energies for the formation of pyranosides and furanosides. As a result of this the action of 1% HCl solution on 2-desoxyribose forms pyranosides, while a hydrogen chloride concentration of 0.1% yields only the more readily formed ion with a furanose ring, analogous to (I).

In examining these reactions it should be remembered that the process may be limited either by the first stage, i.e., the formation of the carbonium ion, or the second stage, i.e., the reaction of this ion with the nucleophilic reagent, depending on the reaction conditions and properties of the reagents.

The hypothesis that the acid itself without a weak nucleophilic agent displaces the equilibrium toward the formation of the furanose form of the sugar is untenable as pyranosides are formed in reactions of sugars in an acid medium with electrophilic agents.

From the above it follows that the formation of pyranosides is characterized by a higher activation energy than the formation of furanosides; as a result of this, the preparation of furanosides requires such mild conditions (a weak nucleophilic reagent, a low temperature, and a low acid concentration) that the activation energy for the formation of furanosides is reached, while that for the formation of pyranosides is not reached.

SUMMARY

1. A mechanism is put forward for the Fischer reaction.

2. The mechanism proposed determines the conditions for the preparation of alkyl furanosides and alkyl pyranosides.

LITERATURE CITED

1. F. Shafizadeh, Adv. carb. chem. 13, 42 (1958).
2. G. R. Barker, D. F. Shaw, J. Chem. Soc. 1959, 584.
3. H. Zinner, Naturw. 46, 531 (1959).
4. C. A. Bunton, T. A. Lewis, D. A. Llewellyn, C. A. Vernon, J. Chem. Soc. 1955, 4419.
5. J. Mills , Adv. carb. chem. 10, 1 (1955).
6. H. C. Brown, I. H. Brewster, H. Shechter, J. Am. Chem. Soc. 76, 467 (1954).
7. Ya. L. Gol'dfarb, L. I. Belen'kii, Usp. khim. 29, 486 (1960).
8. G. P. Ellis, J. Honeyman, Adv. carb. chem. 10, 95 (1955).
9. W. Overend, Adv. carb. chem. 8, 95 (1953).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

MISSING PAGES ARE INDEX PAGES
WHICH HAVE BEEN PHOTOGRAPHED
AT THE BEGINNING OF THE VOLUME(S)

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. –Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
Life Sciences		Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
Life Sciences		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
Life Sciences		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
Earth Sciences		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
Earth Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
Earth Sciences		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
Mathematics		Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
Physics		Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
Physics		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (in English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1 1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1 1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1 1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i teoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.